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# Complex metal halides in fused alkali nitrates

Marlowe LeRoy Iverson  
*Iowa State College*

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COMPLEX METAL HALIDES IN  
FUSED ALKALI NITRATES

by

Marlowe LeRoy Iverson

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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## INTRODUCTION

The concept of dissociation of electrolytes has played an important part in the development of the theory of electrolytic solutions. The view regarding the extent of association in aqueous solution of electrolytes has varied considerably since the first postulates of Arrhenius were presented. The present view in aqueous solutions is that complete dissociation is the exception rather than the rule and that for most electrolytes some interaction is occurring which one refers to as association or ion pair formation (1). Most of the theoretical and experimental investigations of electrolyte solutions apply only to dilute or moderately concentrated solutions.

Fused salts are often referred to as materials having a quasi-crystalline ionic lattice or as highly concentrated solutions of an electrolyte. The behavior of some fused salts can be predicted from a consideration of their crystalline structure and their behavior in aqueous solutions.

The question of the nature and stability of complex ions in solutions of electrolytes has been studied extensively. It is known that the mass association constant for a complex ion depends upon the nature of the solvent and the temperature. The solvent effect is attributed mainly to the dielectric constant of the solvent and the extent of solvation. The small amount of knowledge of these two solvent factors

and the nature of the interactions among ions in a fused salt makes any estimate on theoretical grounds of the degree of association questionable. Thus one must depend at present on experimental observations for indications of complex ions in fused salts.

The common concept of a complex ion is that of a central atom surrounded by a number of usually more negative atoms in a more or less regular configuration. Complex ions in solution generally enter into chemical reactions as units. If this is not true for at least one chemical reaction of a given ion, then it is usually mere inference that one refers to it as a chemical entity, although a compact grouping in a crystal is often used to define a complex ion (2). Two ions held together in a less rigid manner are called ion pairs. Complex ions and ion pairs, produce similar effects in the properties of solutions. These effects are generally attributed to association. Our present state of knowledge of fused salts is not sufficient for one to give the microscopic cause for the association effects observed in many systems.

There is considerable experimental evidence for the existence of fairly stable complex ions in fused salts. Most of this is qualitative in nature because of the difficulty encountered in applying the more direct methods for studying association. However the evidence is substantial enough that one should expect to find effects of complex ions in the chemical as well as the physical behavior of fused salts.

This thesis involves two complementary studies in fused salts. The alkali nitrates are often used in the study of the properties of pure fused salts and the solution behavior of fused salts. The objectives of this investigation are to study some solubility relationships and reaction kinetics using a mixture of alkali nitrates as a solvent for inorganic salts. First, solubility relationships at different temperatures should yield quantitative values for thermodynamic properties of complex ions. Second, a kinetic study of a reaction should yield a mechanism which may involve ions, including complex ions, as reactive species.

## REVIEW OF PREVIOUS WORK

## Association of Ions in Fused Salts

The underlying principles of association of ions have stimulated several investigations in the study of fused salts. Investigations of different motivation have also yielded conclusions regarding association.

Many investigations of fused salts have been concerned with the measurement of some physical property of pure fused salts and binary mixtures of fused salts. In the study of mixtures, the deviations from ideality of the measured property are attributed in many cases to a change in the degree of association.

Physical properties whose deviations from ideality have been attributed to association effects include surface tension (3, 4), conductivity (5, 6, 7), electromotive force (8, 9, 10), and freezing point depression (11, 12, 13, 14, 15). The variation in solubilities of metals in their own fused halides has been attributed to varying degrees of association of the fused halide (5, 16) and conclusions regarding complex ion formation have resulted from spectrophotometric (17) and chromatographic (18) studies in fused salts.

Conductivity is an extensive property which is often studied to gain a better understanding of the structure of matter. The classification of pure molten salts into good

and poor conductors, according to Biltz and Klemm (19), determines their structure in this sense: In these extreme cases, they are either ionic or molecular liquids. The other effects that can simulate incomplete dissociation cannot account for the large difference in conductivity between a molten salt which is a good conductor and one which is an insulator. For the many salts which fall in between, a quantitative interpretation of the numerical values found for the conductivity has not been achieved except for certain systems. Duke, Laity, and Owens (20) have shown that a combination of conductivity, density and transport number data can be used to study the structure of fused salts. In this case the combination of the above data leads to evidence for complete dissociation in fused silver nitrate and sodium nitrate.

Bloom and Heymann (6) treated fused salts as very disordered salts and thus reasoned that certain features of the temperature dependence of conductivity would be indications of constitutional changes such as increased dissociation. If a log plot of conductivity versus the reciprocal of the absolute temperature is non-linear, then one has evidence for constitutional changes in the salt. This non-linear dependence was usually observed for salts which were more likely to be associated in the fused state. For mixtures of fused salts, a maximum in the heat of activation for conductivity versus composition relationship indicates the existence of



complex ions in appreciable quantities in the system. The increase in the heat of activation results from the heat of dissociation of the complex. A maximum was observed in the  $\text{CdCl}_2 + \text{KCl}$  system at a composition corresponding to  $\text{CdCl}_2 + 4\text{KCl}$ . This was interpreted as proof of the existence of the complex ion,  $\text{CdCl}_6^{4-}$ , in appreciable concentration. Other binary systems, including those in which a solid phase compound is indicated by the phase diagram, have been investigated in this manner by Bloom et al. (21). In many of these systems the isotherms of equivalent conductance and molar volumes undergo considerable deviation from linearity indicating a greater degree of short range order or ion association in the molten mixtures. The existence of complex ions is proved on the basis of the heat of activation criteria in only two systems. These are  $\text{PbCl}_2 + \text{KCl}$  and  $\text{CdCl}_2 + \text{KCl}$ .

Cryoscopy is a valuable investigative tool as it is essentially a method by which one can count the number of particles produced by a given quantity of a substance when it is dissolved in another substance. Such information can often be used to determine molecular weights and also the extent of association of a substance in a particular solvent. Cryoscopic data are interpreted (22) using the equation

$$\frac{d \ln a}{dT} = \frac{\Delta H_f}{RT} \quad (1)$$

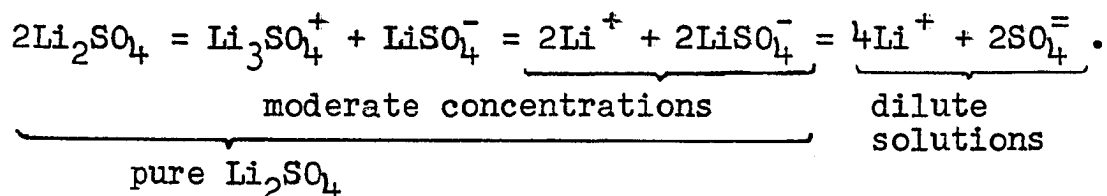
where  $a$  is the activity of the solvent,  $T$  the absolute temperature,  $R$  the gas constant per mole and  $\Delta H_f$  the heat of fusion per mole of pure solvent. The Raoult-Van't Hoff law follows:

$$\Delta T_i = \frac{\nu_i R T_o^2}{1000 L_o} m_i \quad (2)$$

where  $\Delta T_i$  is the freezing point depression due to the addition of solute  $i$ ,  $m_i$  is the concentration of the solute,  $T_o^2$  the freezing point of the pure solvent,  $L_o$  the heat of fusion per gram of solvent and  $\nu_i$  the number of ions into which a molecule of solute  $i$  dissociates. Many claims regarding the extent of association in fused salts have resulted from freezing point depression studies of fused salt solutions.

Goodwin and Kalmus (11) determined the heats of fusion of a large number of salts by calorimetric methods and also carried out some freezing point depression studies. They presented thermodynamic proof that the addition of an ion identical to a solvent ion does not alter the freezing point of the solvent if it is highly dissociated. The behavior of a solute which dissociates into ions, one of which is present in small amounts due to dissociation of the solvent, is illustrated by the halogen acids in water. The freezing point depression in this case corresponds to nearly two particles per mole of acid for dilute solutions (23). Situations analogous to these two cases have been observed in fused salts.

Kordes and associates (13) have studied the cryoscopic behavior of lithium sulfate as a solvent and a solute. They presented the following scheme to represent the molecular structure of fused lithium sulfate under varying conditions:



The various equilibria were based on the following observations. For dilute solutions of lithium sulfate in molten potassium nitrate, the freezing point depression shows the behavior required by three particles per mole up to about one tenth molal. This indicates complete dissociation of lithium sulfate. For the pure salt, cryoscopic studies of sulfates, including those of barium, strontium, calcium, potassium and others, show a freezing point depression corresponding to two (three for  $\text{K}_2\text{SO}_4$ ) particles per mole. The sulfates must dissociate, and in addition the sulfate ion must cause a lowering of the freezing point. Therefore the sulfate concentration in the pure  $\text{Li}_2\text{SO}_4$  must be small. For the intermediate concentration ranges, the eutectic melts with  $\text{SrSO}_4$ ,  $\text{BaSO}_4$  or  $\text{PbSO}_4$  indicate that lithium sulfate dissociates into two particles, neither of which is sulfate and so the ions,  $\text{Li}^+$  and  $\text{LiSO}_4^-$ , are assumed present.

The structure postulated for lithium sulfate is analogous to that postulated for fused mercuric bromide by Jander (24).

This worker represents the structure of fused mercuric bromide as



on the basis of cryoscopic studies and studies of reactions in this solvent. It is noted that mercuric bromide is a poor conductor of electricity in the fused state whereas molten lithium sulfate is undoubtedly highly dissociated.

Very few calculations of the chemical equilibria postulated to exist in fused salts have been made although there are, as noted above, many indications of association. Flood (25) has pointed out that the calculation of chemical equilibria in fused salts at present involves many uncertain assumptions, due to the fact that our knowledge of the thermodynamic properties of fused salts is still very limited. For example, reliable data on heats of fusion and specific heats in the fused state are scarce.

Van Artsdalen (15) has calculated chemical equilibria from freezing point depression studies using fused sodium nitrate as the solvent. Van Artsdalen first showed that a number of simple salts including some oxy-acid salts are stable and evidently ideal in this solvent up to concentrations of one-tenth molal. The ideality is indicated by the fact that the plots of freezing point depression against concentration are linear for dilute solutions and that the values

for the heat of fusion of sodium nitrate calculated from the slope of these plots agree well with the calorimetrically measured value of Goodwin and Kalmus (11). Van Artsdalen points out that, in the absence of complex ion formation, it is expected that solutions of ions in an ionic melt should be much more nearly ideal than aqueous solutions, for the ions of a salt will resemble ions of another salt much more than they resemble water or other polar molecules.

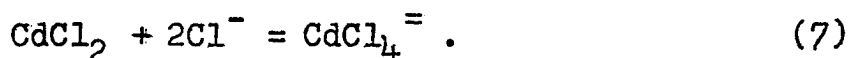
Some of the salts which are apparently ideal in fused sodium nitrate are lead nitrate, the chlorides of calcium, strontium and barium and the chloride, carbonate, sulfate, bromate, tungstate and molybdate salts of sodium.

Several salts show pronounced deviations from ideality in lowering the freezing point of sodium nitrate. These salts,  $\text{PbCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{CdBr}_2$ , behave as though there are considerably less than three foreign particles per molecule. In addition, the freezing point of a sodium nitrate solution containing 0.627 m NaCl actually increases upon the addition of small amounts of cadmium chloride. Van Artsdalen assumed that the deviations were due entirely to incomplete dissociation and complex ion formation. On this basis he calculated constants for the various equilibria which one might postulate to exist in these solutions. He first attempted to calculate constants for the reactions





using  $\text{CdCl}_2$  as an example. However the dissociation constants were found to be markedly concentration dependent. He found that his data could be explained if he calculated equilibrium constants for the reactions



He therefore concluded that although the species  $\text{CdCl}^+$  and  $\text{CdCl}_3^-$  may be formed as intermediates, they were not present in appreciable concentrations and that the important species were those containing an even number of halide ions. The values given for the various association constants are given in Table 1. The constant  $\beta_n$  is defined as

$$\beta_n = \frac{(\text{MX}_n^{2-n})}{(\text{M}^{++})(\text{X}^-)^n} \quad (8)$$

where M is the divalent metal, X is the halide, and the concentration units are moles per 1000 grams of solvent.

The work of Van Artsdalen is one of the very few published involving calculations of chemical equilibria in relatively dilute fused salt solutions.

The association constants for some metal halide complexes in aqueous solutions have been determined by solubility

Table 1. Association constants in molten  $\text{NaNO}_3$  ( $305.8^\circ\text{C}$ )

Salt	$\beta_2$	$\beta_4$
$\text{PbCl}_2$	30	(6)
$\text{CdCl}_2$	320	1410
$\text{ZnCl}_2$	380	1940
$\text{CdBr}_2$	2900	—

methods. Jonte and Martin (26) obtained thermodynamic data for the  $\text{AgCl}_2^-$  complex by measuring the increase in solubility of  $\text{AgCl}$  with addition of chloride ion. King (27) used solubility data of cadmium hexacyanoferrate (III) in solutions containing varying amounts of chloride ion to calculate thermodynamic data for the complex ions  $\text{CdCl}^+$ ,  $\text{CdCl}_2$  and  $\text{CdCl}_3^-$ .

This investigation will involve studying the solubility of slightly soluble metal chromates in a fused nitrate solvent containing varying amounts of possible complexing anions.

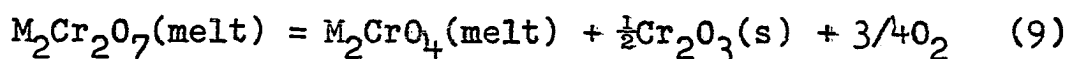
#### Reactions and Reaction Kinetics in Fused Salts

There is little information available on reactions in fused salts and even less on kinetic studies of reactions in fused salts.

Norman and Johnstone (28) studied the catalytic action of ionic type melts upon the decomposition of  $\text{C}_2\text{H}_2$  and the

dehydrogenation of ethyl alcohol. They mention that the studies of catalysis by fused salts in the past have been confined to reactions such as Friedel-Crafts, polymerization, and halogenation in molecular type melts. They conclude that information concerning the degree of dissociation of the various ionic type melts is needed in order to be better able to predict catalytic effects.

Several studies have revealed interesting information about the thermal stability of the oxygen bridge of anions like  $S_2O_7^{=}$  and  $Cr_2O_7^{=}$  in their molten salts. Flood and Maun (29) have studied pyrosulfates which decompose to give an equilibrium concentration of sulfate ion in the melt and an equilibrium pressure of sulfur trioxide. They found that in general the stability of the pyrosulfates decreases with decreasing radius and increasing polarizing power of the cations present. They suggested that cations such as  $Pb^{++}$  polarize the  $SO_3$  group to the extent that it cannot maintain an oxygen bridge. They also investigated the equilibrium reaction



where  $M^+$  was either  $Na^+$ ,  $K^+$  or  $Tl^+$  or mixtures of two. Again the stability of the oxygen bridge was less with decrease in cation radius (30).

Rate studies in fused salts have been mainly studies on the decomposition of pure fused salts. Freeman (31) studied



the decomposition of  $\text{NaNO}_3$  and the reverse reaction between  $\text{NaNO}_2$  and oxygen by weight loss methods.  $\text{NaNO}_3$  was found to decompose slowly at  $600^\circ\text{C}$  and rapidly at temperatures greater than  $756^\circ\text{C}$ . Analysis of the temperature effect on the rate of the decomposition of  $\text{NaNO}_3$  and the heterogenous reaction between  $\text{NaNO}_2$  and  $\text{O}_2$  led him to postulate that the reaction steps were



It is observed that bromide is oxidized in a fused alkali nitrate solvent containing dichromate and lead ions around  $300^\circ\text{C}$ . Very little bromide is oxidized unless both the latter ions are present. One way of studying this reaction is to sweep out the bromine from the solution with an inert gas as it is produced. Preliminary experiments of this type were carried out and some of the results are shown in Figure 1, where the amount of bromine evolved is plotted against time. The top curve represents the rate at which bromide is oxidized in a nitrate solution containing  $\text{Cr}_2\text{O}_7^{=}$  and  $\text{Pb}^{++}$  ions. It was found that metal ions like  $\text{Cd}^{++}$  and  $\text{Zn}^{++}$ , added to the above solution at the start of the reaction, retarded the rate of bromine evolution. One possible explanation for this retarding effect is the formation of a less reactive cadmium

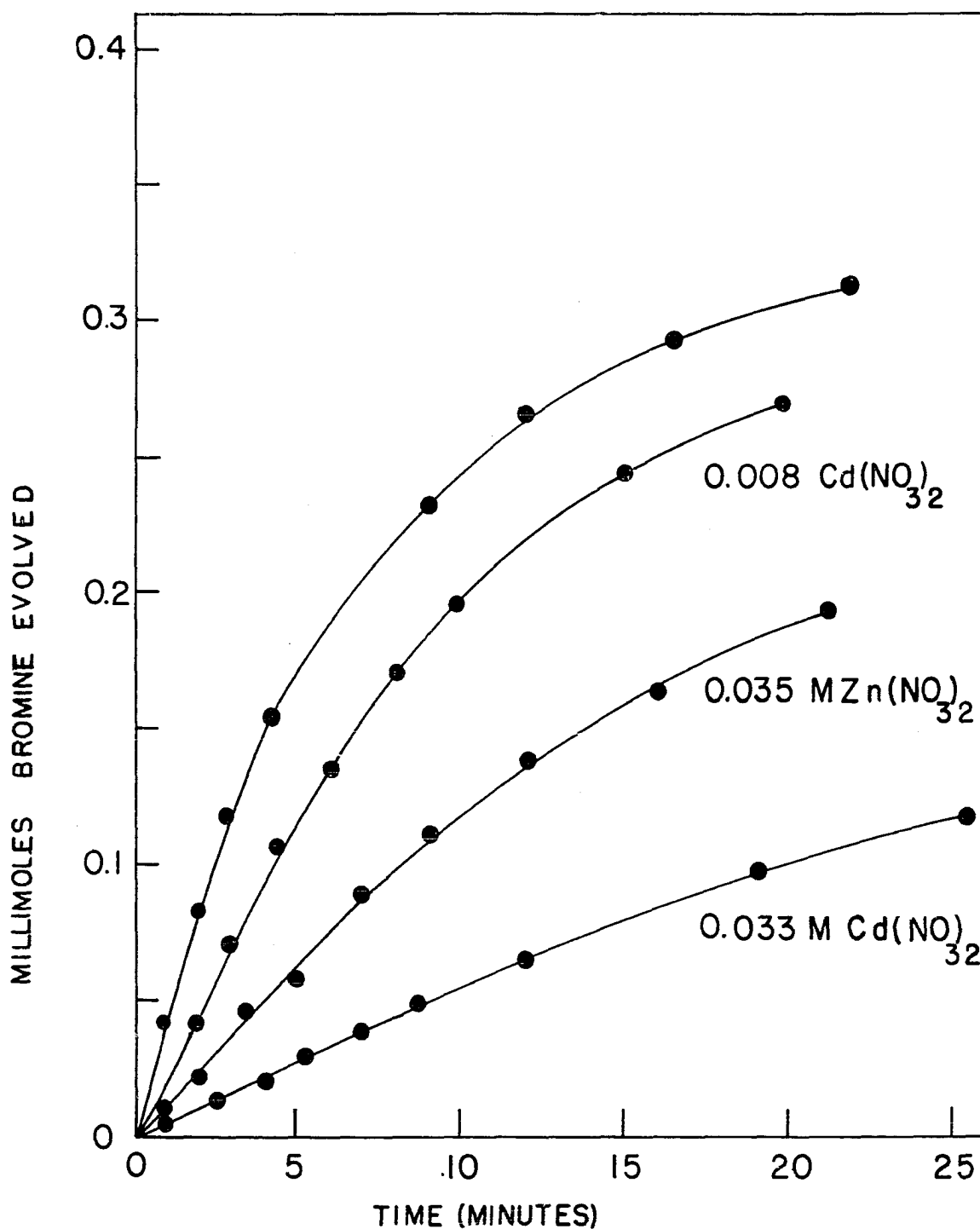


Figure 1. Rate of bromide oxidation in solution containing 0.012 m  $K_2Cr_2O_7$  and 0.035 m  $Pb(NO_3)_2$ . Solvent,  $LiNO_3$ - $NaNO_3$ - $KNO_3$  eutectic; 200°C;  $N_2$  sweep gas

or zinc bromide complex ion. To prove this, a more complete understanding of the oxidation reaction is needed.

One of the difficulties noted in studying the oxidation reaction involving  $\text{Br}^-$ ,  $\text{Cr}_2\text{O}_7^{=}$ , and  $\text{Pb}^{++}$  ions was that of determining the  $\text{Cr}_2\text{O}_7^{=}$  and  $\text{Pb}^{++}$  concentrations since a precipitate always formed when these ions were present in the solution. The precipitate which forms is  $\text{PbCrO}_4$  so that some reaction between the dichromate ion and the nitrate ion of the solvent or some other oxygen source must be taking place. This reaction involving dichromate ion is interesting and requires further investigation for a better understanding. One of the objectives of this thesis is the study of this reaction.

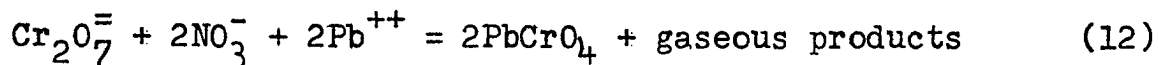
## KINETIC STUDIES

## Features of the Dichromate Reaction

A bright colored solution of potassium dichromate in a fused alkali nitrate is to all appearances a stable solution. The lack of any apparent reaction is indicated by the fact that ideal freezing point behavior is reported for potassium dichromate dissolved in fused sodium nitrate as the solvent (15) and that no irregularities are indicated by the conductivity isotherms of the fused potassium dichromate + potassium nitrate system (32).

A precipitate usually forms immediately, when a lead salt, e.g. lead nitrate, is added to a solution of potassium dichromate in a solvent consisting of a eutectic mixture of sodium nitrate and potassium nitrate. The precipitation is complete after a period of time varying from one hour to several days depending upon the concentrations and other conditions involved. Essentially all of the dichromate is precipitated as the chromate. The composition of the reddish-yellow precipitate is determined by chemical analysis of the dichromate solution after adding varying amounts of lead to the solution and waiting for the resulting precipitation to be completed. The concentration of dichromate in the supernatant liquid corresponds to the initial concentration minus one-half the amount of lead which was added (expressed in the

same concentration units). The over-all reaction taking place is



where the gaseous products consist of oxygen and oxides of nitrogen.

The composition of the gaseous products, based upon results obtained by passing the gases through standard alkali, has been found to vary depending upon conditions. Most of the nitrogen is evolved as nitrogen dioxide. This is apparent from the very noticeable brown appearance of the gases evolved and from chemical analysis of the nitrogen dioxide by absorption in standard alkali. In terms of the amount of dichromate added, the amount of nitrogen dioxide evolved usually amounts to 1.4 to 1.8 moles of nitrogen dioxide per mole of dichromate added. This amounts to recovering 70 to 90 per cent of the nitrogen indicated by the stoichiometry of Equation 12 as nitrogen dioxide.

In view of the above reaction, the stability of a 0.026 molal dichromate solution (50 grams of eutectic solvent at 300° C) was checked by bubbling nitrogen through the solution and absorbing the acidic gases in standard alkali. In a period of four hours, during which the solution was continuously flushed with nitrogen, only 0.01 milliequivalents of acid were evolved. This indicated that, although some reaction may be occurring, a dichromate solution is fairly stable and that

the addition of the lead ion must cause the reaction to proceed at a faster rate.

A chromium trioxide solution in the fused alkali nitrate solvent resembles a dichromate solution with respect to this reaction. Lead chromate is precipitated from a chromium trioxide solution at about the same rate as from a dichromate solution of equal concentration. An initial reaction between the solvent and chromium trioxide is uncharacterized.

In addition to the features of the reaction as outlined above, it is known that if potassium bromide is added to a fused alkali nitrate solution containing dichromate and lead ions, bromine is evolved at a rate depending upon the dichromate and lead concentrations and also upon the concentration of other metal ions, notably cadmium and zinc.

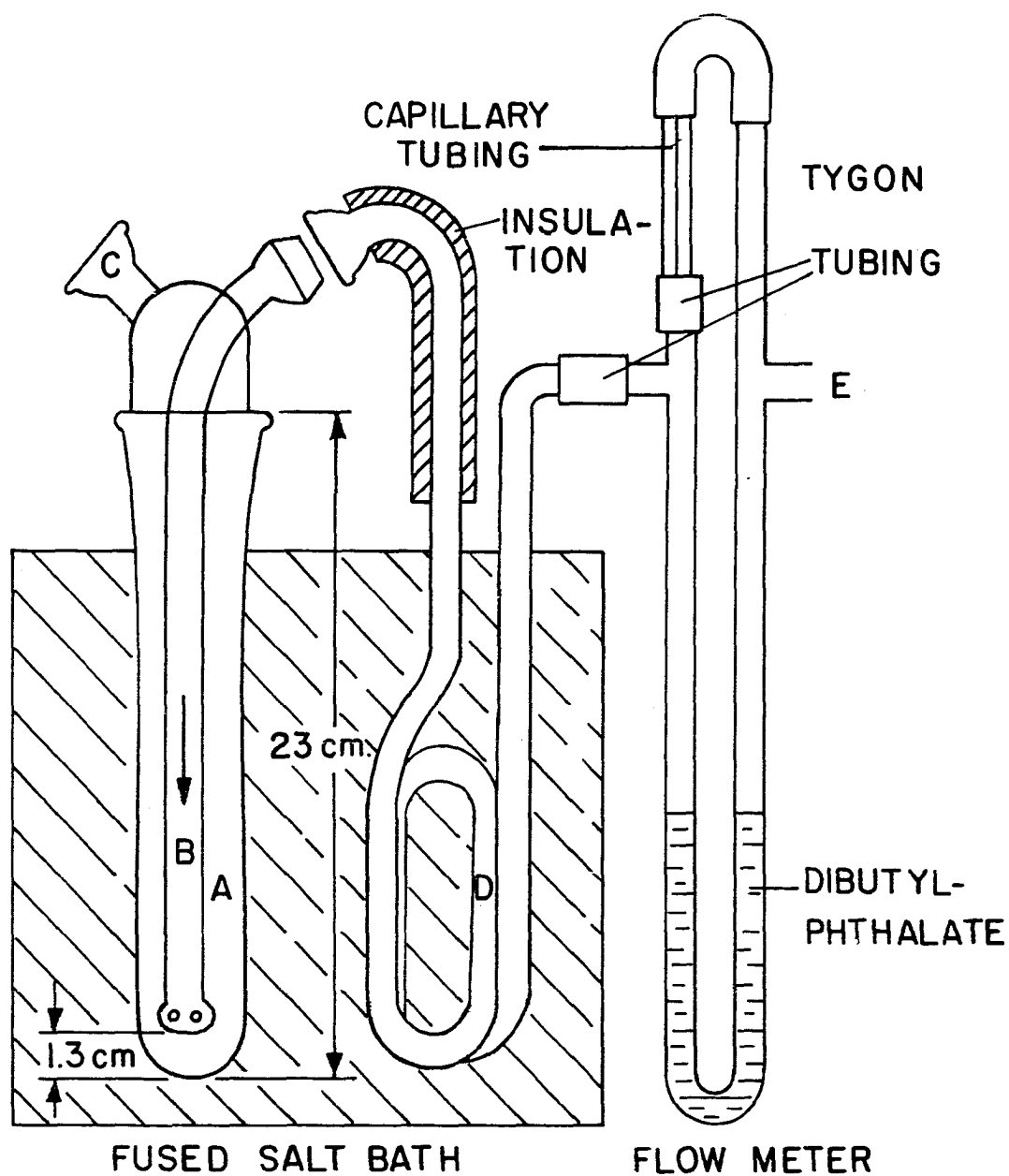
It is indicated above that lead ion is necessary to cause the reaction (12) to take place. Other bivalent metal ions also are effective in promoting this reaction although the rate of the reaction varies considerably depending upon the bivalent metal ion present. For example barium and calcium also precipitate chromate from a dichromate solution but at a much slower rate.

## Experimental

### Rate determinations

A.C.S. reagent grade chemicals were used. All of the rate determinations were made in reaction vessels immersed in a fused salt bath. The fused salt bath consisted of a eutectic mixture of the nitrates of lithium, sodium, and potassium. The fused bath was contained in an insulated enameled iron vessel 11 inches in diameter and 8 inches in depth. The bath was maintained at the desired temperature  $\pm 1^\circ\text{C}$  with a chromel-alumel indicating thermocouple connected to a Brown Potentiometer pyrometer, model 156R16-PS-141 (Minneapolis-Honeywell Regulator Co., Philadelphia, Penn.).

The majority of the experimental runs were carried out in the reaction vessel illustrated in Figure 2. The vessel was made from No. 36 pyrex tubing and standard taper glass fittings. A gas flow meter was attached to the reaction vessel to meter the flow rate of gas (nitrogen or oxygen) used to sweep the solutions before a reaction and also to remove gaseous products and produce a controlled rate of stirring during the reaction. The sweep gases were preheated in the glass coil before entering the reaction vessel. No temperature drop of the reaction solution was detected at the highest flow rate used in this investigation.



A. REACTION VESSEL (I.D.= 31m.m.)

B. INLET TUBE

D. SWEEP GAS HEATER

C. OUTLET

E. TO SWEEP GAS SOURCE

Figure 2. Reaction vessel and flow meter



The reaction vessel outlet was connected to absorbers containing either standard alkali, so that the acidic constituents of the evolved gases could be measured, or a sulfur dioxide solution for collecting bromine when bromide was added to the reaction mixture.

At first it appeared possible to determine the extent of the reaction by analysis of the evolved gases; however a series of experiments showed that the ratio of moles of acid evolved to moles of dichromate reacted varied depending upon the flow rate of the sweep gases and upon the concentration of the dichromate in the solution.

The precipitate formed in this reaction separates rapidly from the solution after the first ten to twenty minutes of reaction time. The precipitate settles sufficiently well so that a preheated pipette can be immersed in the solution and samples sufficiently free of suspended material can be withdrawn. Two or more samples were usually withdrawn and the reaction was studied by following the change in dichromate concentration of the samples. Due to the nature of the reaction, a filtering technique could not be used. To illustrate this some typical results obtained with filtered and non-filtered samples from the same solution are compared in Table 2. The uniformly low results and the lack of precision with filtered samples indicated that the dichromate concentration was changing rapidly during passage through the filter

Table 2. Comparison of dichromate concentration of filtered and non-filtered samples

$\text{Cr}_2\text{O}_7^{=}$ (m)	
Filtered samples <sup>a</sup>	Non-filtered samples
$1.75 \times 10^{-3}$	$3.85 \times 10^{-3}$
1.34	4.04
<u>2.35</u>	<u>3.84</u>
$1.81 \pm 0.32$ ave.	$3.91 \pm 0.09$

<sup>a</sup>The filtered samples were obtained by drawing the solution through a layer of silica gel (28-200 mesh, dried at 110°C) packed between two layers of glass wool.

probably due to the chemical and physical effects of the large surface area of the filtering material.

In view of these and other results, the filtering technique was not used and the samples for the runs were withdrawn simply with a pipette. Each sample as it was withdrawn was held against a white background and observed for particles of suspended precipitate before emptying the entire sample onto a porcelainized plate. If the sample contained some suspended precipitate, it was carefully placed back into the reaction solution and another sample was withdrawn after waiting a minute or two.

The dichromate concentration of the sample was determined by the iodide-thiosulfate method (33). The one-two gram sample was dissolved in 50 milliliters of water. One

gram of potassium iodide was added followed by 10 milliliters of 6N hydrochloric acid. The solution was then titrated to the starch-iodine endpoint with standard 0.01N thiosulfate solution. Duplicate samples usually agreed to within two per cent.

The usual procedure in making a kinetic run was as follows: The reactants were dried for one hour at 110°C and then the desired amounts of each were weighed out. The solvent ( $\text{NaNO}_3 + \text{KNO}_3$  eutectic) was weighed out and melted in two portions in vessels immersed in the fused salt bath. The reactant, potassium dichromate, was dissolved in one portion and the other reactant, usually lead nitrate, was dissolved in the other portion of fused solvent. The solutions were prepared at least an hour and sometimes up to a day before beginning the reaction. The reaction was started by mixing the two solutions together in the reaction vessel. Samples of the solution were then withdrawn at intervals for analysis. Usually six or more samples were withdrawn during a run.

If the kinetic experiment being carried out involved the use of a sweeping gas or mechanical stirring, this agitation had to be stopped during the sampling period. The maximum time required in these cases was never over five minutes. Since the reaction rate varies with agitation, as will be shown, corrections had to be applied for those reactions which were sixty per cent or more complete in less than two

hours by taking into account the reduced rate of reaction during the sampling period.

### Rate effects

The first studies of this reaction were carried out in an open reaction vessel without any stirring. In those experiments, as in most of the succeeding ones, the reaction solution contained an excess of lead ion over dichromate ion. A plot of the logarithm of the total dichromate concentration against time usually gave a good straight line and the pseudo first order rate constant,  $k'$ , was evaluated from the slope of this plot. In addition to the first order dependence in dichromate, an order in lead somewhere between one and two was indicated.

The rate of this reaction varies with the quantity of solution in the reaction vessel or probably more meaningfully with the ratio of the air-solution interfacial area to the volume of the solution. It was observed that the use of a sweeping gas to remove the gases evolved during the reaction also caused an increase in the reaction rate. The dependence of rate on the flow rate of the sweeping gas and on the quantity of solution is shown in Table 3. The reproducibility of the rate constants is about  $\pm 5$  per cent.

If oxygen is substituted for nitrogen as the sweep gas, the same rate increase is observed at the same flow rate as

Table 3. Variation of pseudo first order rate constant with quantity of solution and flow rate of the sweep gas through the solution

Nitrogen sweep gas,  $(\text{Pb}^{++}) = 0.044 \text{ m}$   
 Initial  $(\text{Cr}_2\text{O}_7^{=}) = 0.0030 \text{ m to } 0.0070 \text{ m}$

Total solvent grams	$k' \times 10^5 (\text{sec}^{-1})$ Nitrogen flow rate (liters per minute)			
	0	0.21	0.73	1.70
45	2.6	3.9	6.0	8.1
95	2.1	3.4	4.9	6.9
195	1.7	—	3.8	—

nitrogen. Some other effects are shown in Figure 3 where the dichromate concentration on a logarithm scale is plotted against time. Mechanical stirring of the reaction solution, using an electric motor and a pyrex glass stirring rod, also causes a rate increase. Qualitatively the increase is not as great as that due to a sweeping gas when compared on the basis of the agitation developed in the solution. The presence of additional lead chromate in the solution, freshly precipitated at the start of the reaction, has a very slight effect on the rate.

Due to the heterogeneous character of this reaction, it is apparent that for comparing kinetic data, this reaction must be carried out under carefully controlled conditions. For this reason, additional kinetic runs of this reaction were usually carried out under the following conditions:

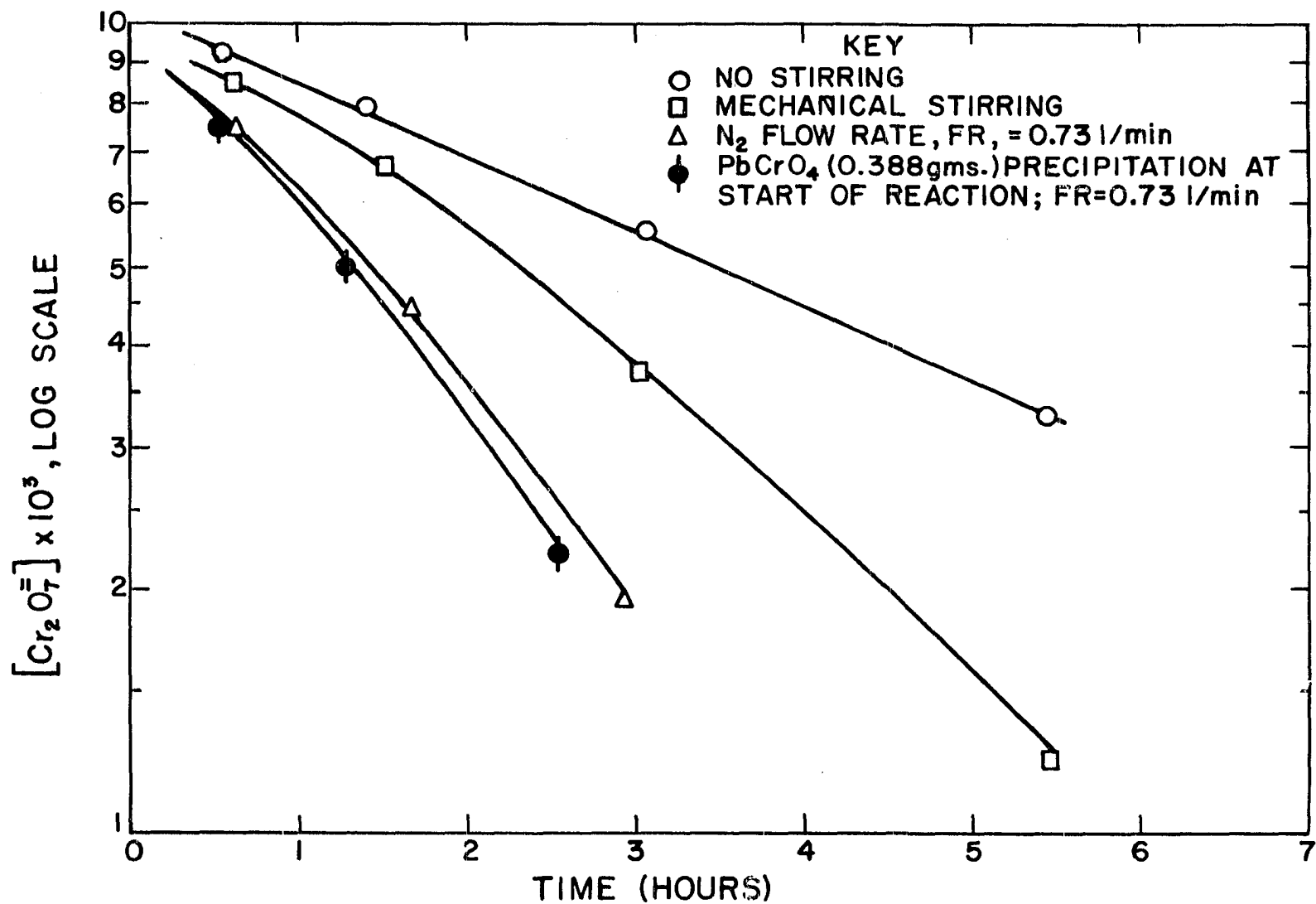


Figure 3. Logarithm dichromate concentration versus time showing rate effects. Initial (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) = 0.012 m, (Pb<sup>++</sup>) = 0.050 m; 50 grams solvent; 300°C

1. A total quantity of 95 grams of solvent was used at the start of a reaction. The total amount of solvent removed during the reaction as samples usually amounted to five grams not including the samples from the last time interval. The error due to this change in quantity of solution was small enough to be neglected.

2. The reactions were carried out using a nitrogen sweep at a flow rate of 0.21 liters per minute. The data obtained without using a sweep gas were not as reproducible as the data obtained at some constant sweep gas flow rate.

#### Rate dependence on lead concentration (300°C)

A series of rate studies were carried out in which the total lead nitrate concentration was varied from 0.012 m to 0.196 m with a total initial potassium dichromate concentration of 0.003 m to 0.004 m. This amounted to an excess of lead ion of 3 to 60 times the dichromate concentration. Except for the runs with lower lead concentrations, the lead could be considered constant during most of the reaction. Plots of the logarithm of the total dichromate concentration versus time gave good straight lines from which pseudo first order rate constants were evaluated. These constants are shown in Table 4.

In order to determine the rate dependence on lead ion concentration, a plot was made of the logarithm of the pseudo

Table 4. Variation of pseudo first order rate constant with lead ion concentration

Initial  $(\text{Cr}_2\text{O}_7^{=}) = 0.0030 \text{ m to } 0.0040 \text{ m}$   
 $\text{N}_2$  flow rate = 0.21 liters per minute  
 95 grams of solvent

250°C		300°C	
$(\text{Pb}^{++})$ m	$k' \times 10^5$	$(\text{Pb}^{++})$ m	$k' \times 10^5$
0.044	$3.0 \pm 0.2$	0.012	0.48
0.094	$8.8 \pm 0.4$	0.021	1.10
		0.023	1.4
		0.044	$3.4 \pm 0.2$
		0.094	$8.9 \pm 0.3$
		0.194	$17.7 \pm 1.0$

first order rate constant versus the logarithm of the lead nitrate concentration. This relationship, shown in Figure 4, shows that the order in lead changes from nearly second order at low lead to nearly first order at higher lead concentrations. The solid curve through the points represents the empirical equation

$$\log k' = A + 2\log(\text{Pb}^{++}) - \log [1 + 47(\text{Pb}^{++})] \quad (13)$$

where A is a constant.

Reliable data to extend the above relationship to higher lead concentrations could not be obtained because the ac-



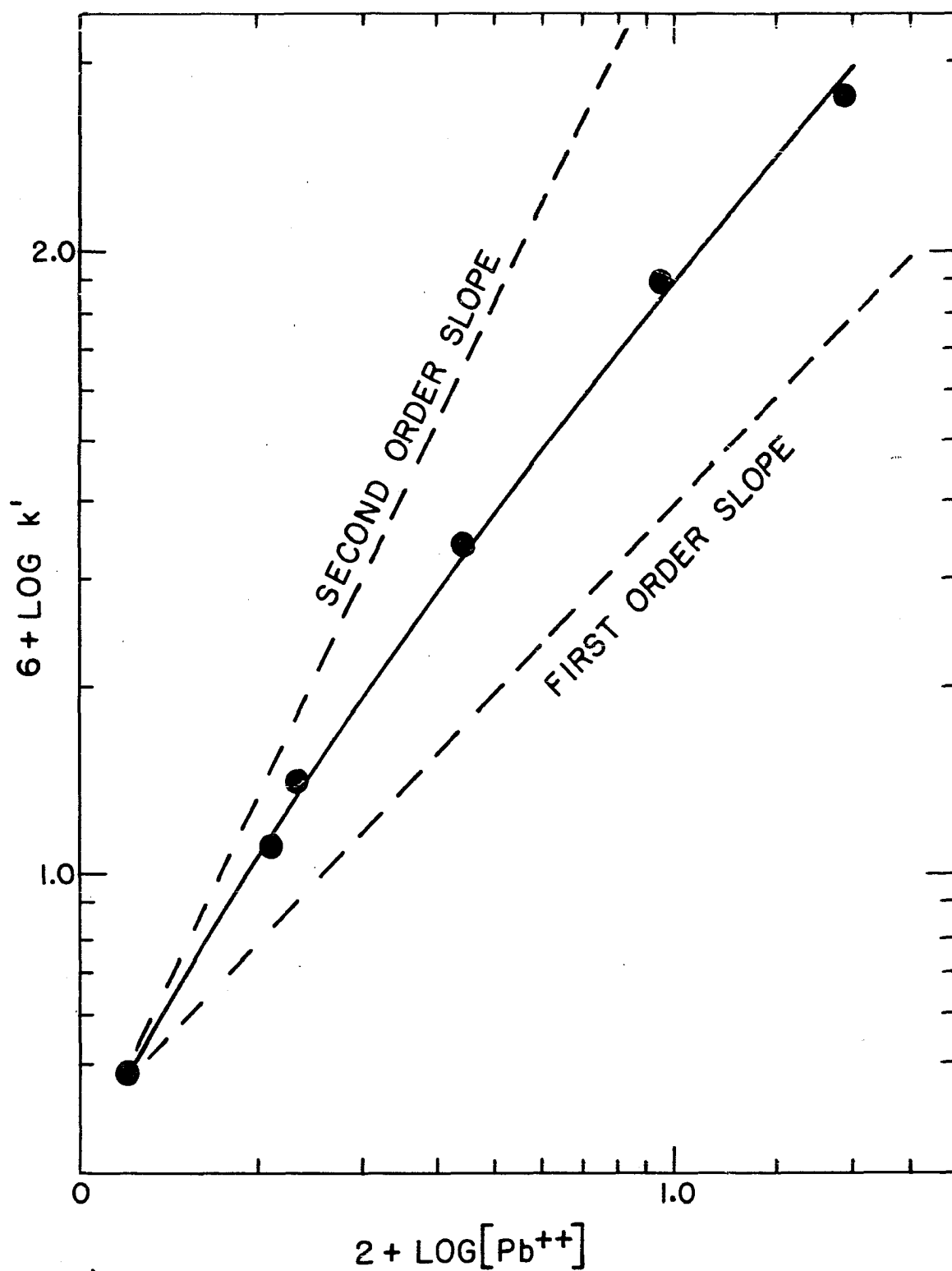


Figure 4. Rate dependence on lead ion concentration. Initial  $(\text{Cr}_2\text{O}_7^{=}) = 0.0050 \text{ m}$ ;  $\text{N}_2$  flow rate = 0.21 liters per minute;  $300^\circ\text{C}$

companying more rapid rate prevented the lead chromate from settling sufficiently for samples to be taken.

Experiments were carried out using an excess of dichromate over lead. Under these conditions, the precipitate does not separate from the solution by gravity well enough to allow accurate determination of the dichromate concentration.

#### Rate dependence on temperature

The temperature effect on the rate of this reaction is very slight as shown by the data in Table 4. The pseudo first order rate constants are compared at two different lead concentrations at 250° and 300°C. The rates for the two temperatures at comparable lead concentrations are equal within the experimental error.

#### Rate dependence on other bivalent metal ions (300°C)

Barium chromate and calcium chromate are also precipitated slowly from a solution of potassium dichromate dissolved in a fused sodium nitrate-potassium nitrate eutectic solvent. Both barium and calcium chromate are only slightly soluble in this solvent although both are more soluble than lead chromate.

The following experiments were carried out in order to compare the rates for the reactions involving those three

metal ions. Solutions containing 0.026 m  $K_2Cr_2O_7$  and 0.10 m bivalent metal ion in 45 grams of solvent were prepared in 8 inch test tubes immersed in the fused salt bath. The rate of the reaction without stirring was followed in the usual manner over a two week period. The large difference in the rates is shown in Table 5. A comparison of the lead and barium rates was also made by carrying out the reactions in 95 grams of eutectic solvent in the reaction vessel with no stirring. The starting concentrations were  $(Cr_2O_7^{=}) = 0.0050m$ ,  $(Ba^{++}) = 0.10$ , and  $(Pb^{++}) = 0.050$ . The pseudo first order rate constants from these experiments are included in Table 5.

It is apparent from the data in Table 5 that the rate of the dichromate reaction is considerably less when other metal ions are substituted for  $Pb^{++}$ . Other cations which form slightly soluble chromates such as  $Cd^{++}$  and  $Ag^+$  (solubilities of the order of  $CaCrO_4$ ) do not precipitate chromate ion from a dichromate solution at rates greatly different from calcium. Rate data for solutions containing equal molar mixtures of  $Pb^{++}$  and either  $Ba^{++}$  or  $Cd^{++}$  were also obtained. The rate constants for these experiments are included in Table 5.

#### Chloride and bromide effect on rate (300°C)

The rate of the dichromate reaction in fused sodium nitrate-potassium nitrate eutectic is affected by the addition of either bromide or chloride ions. The bromide effect is

Table 5. Variation of the pseudo first order rate constant with kind and concentration of bivalent metal ion in solution (300°C)

Bivalent metal salt		$k' \times 10^5$ (Sec <sup>-1</sup> )
Salt	Concentration(m)	
Initial ( $\text{Cr}_2\text{O}_7^{=}$ ) = 0.026 m, 45 grams solvent, test tube reaction vessel.		
$\text{Pb}(\text{NO}_3)_2$	0.084	1.30
$\text{Ba}(\text{NO}_3)_2$	0.094	0.045
$\text{Ca}(\text{NO}_3)_2$	0.094	0.013
Initial( $\text{Cr}_2\text{O}_7^{=}$ ) = 0.0050 m, 95 grams total solvent, reaction vessel, no sweep gas.		
$\text{Pb}(\text{NO}_3)_2$	0.046	2.08
$\text{Ba}(\text{NO}_3)_2$	0.098	0.28
Initial ( $\text{Cr}_2\text{O}_7^{=}$ ) = 0.0050 m, 95 grams solvent, N <sub>2</sub> flow rate of 0.21 liters per minute through reaction vessel.		
$\text{Pb}(\text{NO}_3)_2$	0.046	3.40
$\text{Pb}(\text{NO}_3)_2$ +	0.046	2.50
$\text{Ba}(\text{NO}_3)_2$	0.050	
$\text{Pb}(\text{NO}_3)_2$ +	0.046	2.80
$\text{Cd}(\text{NO}_3)_2$	0.050	

quite different from the chloride effect. One finds a very marked accelerating effect due to bromide ion but with addition of chloride ion, a marked retarding effect on the rate of the reaction is found. However, in the case of bromide,

bromine is evolved during the reaction whereas no trace of chlorine or chloride is found in the evolved gases.

With the addition of bromide up to moderate concentrations, the reaction proceeds rapidly until all of the bromide is evolved as bromine and then the reaction proceeds at a normal rate. The amount of bromide which can be oxidized corresponds closely to one mole of bromide oxidized per one mole of dichromate reacted, i.e. converted to chromate. For example, all of the dichromate is precipitated from solution in less than fifteen minutes if the initial concentrations are 0.012 m  $\text{K}_2\text{Cr}_2\text{O}_7$ , 0.005 m  $\text{Pb}(\text{NO}_3)_2$  and 0.6 m KBr.

The rate retarding effect of chloride could be evaluated more quantitatively. A series of rate studies were carried out involving different concentrations of potassium chloride. The chloride concentration was varied from 0.25 m to 1.0 m and the starting concentrations of potassium dichromate and lead nitrate were 0.005 and 0.050 molal respectively. The pseudo first order rate constants evaluated from the log dichromate versus time plots at the different chloride concentrations are shown in Table 6. At the highest chloride concentration employed, the rate of the reaction was approximately one-eightieth the rate when no chloride ion was present.

Table 6. Variation of pseudo first order rate constant with chloride concentration

300°C, initial  $(\text{Cr}_2\text{O}_7^{=}) = 0.0050\text{m}$ , 95 grams of solvent

KCl m	$k' \times 10^5$
(Pb <sup>++</sup> ) = 0.048 m, N <sub>2</sub> sweep rate 0.21 liters per minute	
0.00	3.60
0.25	0.91
0.50	0.31
0.75	0.18
1.00	0.043
(Ba <sup>++</sup> ) = 0.098 m, no stirring	
0.00	0.028
1.00	0.035

### Discussion

#### Proposed mechanism of the dichromate reaction

The explanation for the kinetic behavior of the dichromate ion in fused alkali nitrates apparently lies in the manner in which dichromate ion is depolymerized. The explanation which one might propose must be consistent with the following experimental facts:

- (1) The various rate effects due to stirring, sweep gas flow rate, etc.
- (2) The first order dependence in dichromate ion and the changing order, from one to two, in lead ion.
- (3) The dependence of the rate on the specific bivalent metal ion in solution.
- (4) The marked stabilization of a dichromate and lead nitrate solution when chloride ion is added and the very small effect of chloride on the barium-dichromate reaction rate.
- (5) The small temperature dependence of the reaction rate.
- (6) The bromide accelerating effect.

During the early part of the investigations, two explanations different from the one proposed in this thesis were considered for the dichromate ion behavior. These two rejected explanations will be discussed briefly. They are:

- (1) The dichromate ion is hydrolyzed by a very small amount of residual moisture in the fused salt.
- (2) The dichromate ion dissociates into chromate ion and chromium trioxide which reacts with nitrate ion.

The hydrolysis explanation was abandoned because it did not appear reasonable that the amount of water in the solution could be kept constant despite different treatments applied to the solutions. The fact that the kinetic data could be

reproduced whether or not the solutions were dried by bubbling an inert dry gas through them for twenty hours before mixing the solutions implies that either the water content is constant or that water is not important either as part of an equilibrium or in a kinetic step<sup>1</sup>.

The second explanation assumes one of the following reactions to be rate controlling.



If the first reaction is considered as an equilibrium and the second reaction rate controlling, the expression for the rate of reaction of dichromate can be written as

$$\frac{d(\text{Cr}_2\text{O}_7^{=2})}{dt} = \frac{k_1 K_e (\text{Cr}_2\text{O}_7^{=2}) (\text{Pb}^{++})}{K_s} \quad (16)$$

where  $K_e$  is the equilibrium constant for the equilibrium reaction and  $K_s$  is the solubility product of lead chromate and  $k_1$  is the pseudo first order rate constant involving the nitrate ion concentration. Although this rate expression is in agreement with dichromate ion and lead ion dependence at

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<sup>1</sup>Evacuating the solutions several hours under high vacuum before mixing the reagents did not have any noticeable effect (34).



high lead concentrations, this mechanism does not explain the change to second order in lead at low concentrations and, more important, it does not explain the large effects on the rate due to bubbling an inert gas through the reaction solution.

The effect of agitation is shown in Figure 5 where the pseudo first order rate constant is plotted against sweep gas flow rate. The large rate effect due to bubbling an inert gas through the solution during the reaction is strong evidence for the fact that a gaseous product in equilibrium with the reactants in solution is being removed (35). The fact that the main gaseous products observed in this reaction are nitrogen dioxide, nitric oxide and oxygen does not mean that these are the gases in equilibrium with the reactants for these could result from the further decomposition of the actual gaseous product. That the observed gases are not in equilibrium with the reactants in solution is indicated by the fact that the reaction proceeds at the same rate whether the gaseous products are removed as the reaction proceeds or whether they are allowed to remain in contact with the solution in a closed system.

The actual gaseous product in equilibrium with the reactants is probably nitrogen pentoxide. This is indicated by the fact that the gaseous products observed are those which result from the decomposition of nitrogen pentoxide (36).

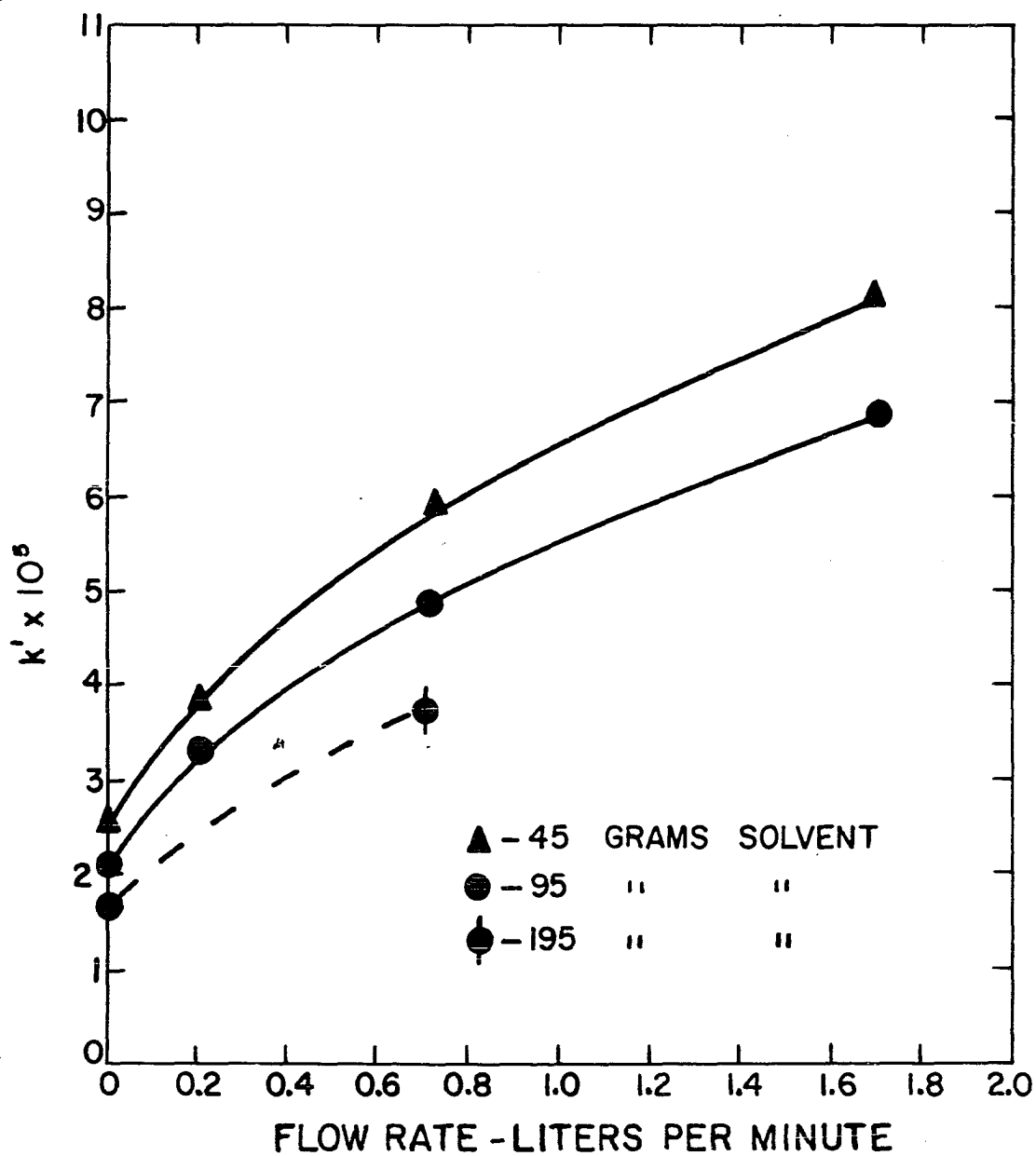
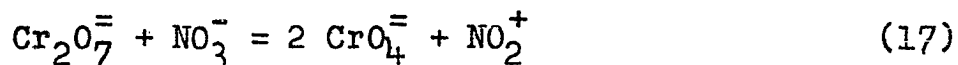


Figure 5. Variation of first order rate constant with quantity of solution and sweep gas flow rate.  
 $(\text{Pb}^{++}) = 0.50 \text{ m}$ ;  $300^\circ\text{C}$

The nature of the reaction also suggests that some nitrogen pentoxide would be formed. One can consider the reactions (14) and (15) or over-all reaction,



as equilibrium processes which, followed by the combination of the nitronium ion with the nitrate ion of the solvent,



give the gaseous product, nitrogen pentoxide. The rate at which dichromate is precipitated then depends upon the rate at which nitrogen pentoxide is removed from the system either by decomposition or by diffusion to the surface and evaporation.

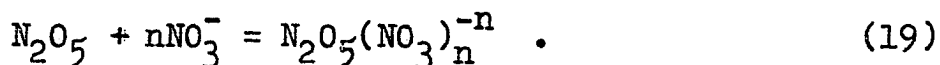
The decomposition of nitrogen pentoxide has been studied extensively. Daniels and Johnston (37) carried out the first complete investigation of gaseous nitrogen pentoxide decomposition in the temperature range 25 to 65°C. The reaction was found to be unimolecular with an activation energy of 24.7 kcal. per mole. Eyring and Daniels studied the decomposition of nitrogen pentoxide in inert solvents (38) and in chemically active solvents (39). In all cases the rate follows the unimolecular formula. In inert solvents, such as liquid nitrogen dioxide, chloroform, and liquid bromine, the first order rate constant does not vary greatly from its

value in the gaseous phase at the corresponding temperature. In chemically active solvents such as 96 per cent nitric acid the decomposition proceeds very slowly. This was explained on the assumption of a stable solvated nitric acid-nitrogen pentoxide molecule in equilibrium with the nitrogen pentoxide. Ingold and Millen (40) have established that nitrogen pentoxide is essentially completely dissociated in nitric acid at  $-15^{\circ}\text{C}$ .

Other evidence for the stabilizing effect of concentrated nitric acid on nitrogen pentoxide has resulted from kinetic studies of the thermal decomposition of nitric acid in the liquid phase. Tait et al. (41) estimate that three per cent of the nitrogen pentoxide in concentrated nitric acid exists in the molecular form at  $65^{\circ}\text{C}$  on the basis of kinetic data. Robertson et al. (42) suggest that the unimolecular decomposition of nitrogen pentoxide or the interaction of its products,  $\text{NO}_2^{+}$  and  $\text{NO}_3^{-}$ , plays a significant role in the rate-determining step in the decomposition of concentrated nitric acid. Both neutral salts and nitrates (to a lesser extent) decrease the rate of decomposition. The reason for this salt retarding effect is not clear.

One can only speculate as to the equilibrium that might exist between nitronium ion, nitrate ions and nitrogen pentoxide in a fused alkali nitrate salt. The high concentration of nitrate ions should favor the formation of  $\text{N}_2\text{O}_5$  and pos-

sibly more complex ions may be formed by the solvation reaction:



This may stabilize  $\text{N}_2\text{O}_5$  with respect to decomposition and this along with the very small total concentration may explain the small amount of  $\text{N}_2\text{O}_5$  lost by decomposition in solution. The possible transport of  $\text{N}_2\text{O}_5$  to the surface in the form of nitronium ions or the more complex species might account for the evidently large mass transfer effect. The conditions at the surface may be more favorable to the formation of an  $\text{N}_2\text{O}_5$  molecule which escapes to the gaseous phase and decomposes almost immediately.

The total loss of nitrogen pentoxide can be expressed as a sum of the loss due to decomposition in situ and the loss due to mass transfer. If the unimolecular process is assumed for the decomposition step in solution and the mass transfer process is represented as a function,  $f$ , of the concentration gradient of nitrogen pentoxide at the surface (43), the following rate expression is obtained.

$$-\frac{d(\text{N}_2\text{O}_5)}{dt} = k_2(P_s) + f(P_i, P_g) \quad (20)$$

where  $k_2$  is the unimolecular specific rate constant for the decomposition,  $P_s$  is the  $\text{N}_2\text{O}_5$  pressure in the bulk of the solution,  $P_i$  is the  $\text{N}_2\text{O}_5$  pressure at the interface and  $P_g$  is

the pressure of  $N_2O_5$  in the gaseous phase. Now suppose that the evaporation step is the slow mass transfer step. The pressure  $P_i$  can be considered proportional to the solution pressure  $P_l$  and, under the conditions of the experiments, the concentration or pressure of  $N_2O_5$  in the gaseous phase may be considered negligible due to the rapid decomposition of  $N_2O_5$  and the continuous removal of the gas phase in immediate contact with the solution. These assumptions allow one to combine the decomposition and diffusion terms and express the removal of  $N_2O_5$  from equilibrium as

$$-\frac{d(N_2O_5)}{dt} = k_3(N_2O_5) \quad (21)$$

where  $k_3$  is a proportionality constant containing both the diffusion terms and the unimolecular decomposition constant for nitrogen pentoxide and  $(N_2O_5)$  is its concentration in moles per 1000 grams of solvent. The concentration of nitrogen pentoxide can be expressed as

$$(N_2O_5) = \frac{K(Cr_2O_7^{--})}{(CrO_4^{--})^2} \quad (22)$$

where  $K$  is the equilibrium constant for the combined Reactions 17 and 18. Substitution of this expression into Equation 21 gives the rate expression

$$-\frac{d(N_2O_5)}{dt} = -\frac{d(Cr_2O_7^{--})}{dt} = \frac{Kk_3(Cr_2O_7^{--})(Pb^{++})^2}{K_s^2} \quad (23)$$

where  $K_s$ , the solubility product of lead chromate, and  $(Pb^{++})$  replace  $(CrO_4^{--})$ . This rate expression is in agreement with the behavior observed at low lead concentrations.

The change in order of lead from two at low lead to one at high lead concentrations can be accounted for if one assumes that a stable lead dichromate molecule or complex is formed. The association constant for this complex is given by

$$K_1 = \frac{(PbCr_2O_7)}{(Pb^{++})(Cr_2O_7^{--})} \quad (24)$$

The dichromate concentration can be expressed as

$$(Cr_2O_7^{--}) = \frac{(Cr_2O_7^{--})_t}{1 + K_1(Pb^{++})} \quad (25)$$

Substitution of this expression for the dichromate concentration into the rate Expression 7 leads to the rate expression

$$-\frac{d(Cr_2O_7^{--})}{dt} = \frac{k_4 (Pb^{++})^2 (Cr_2O_7^{--})_t}{K_s^2 [1 + K_1(Pb^{++})]} \quad (26)$$

This expression represents the observed behavior shown in Figure 4 if  $K_1$  is assigned a value of 47. This explanation might have been more convincing if the retarding effect of  $Ba^{++}$  were less than that of  $Cd^{++}$  (Table 5). This would have indicated that the  $Cd^{++}$  is forming a stronger complex with  $Cr_2O_7^{--}$  which one might have expected. However, the opposite effect is observed and one is hesitant to attribute the

greater retarding of  $\text{Ba}^{++}$  to its tendency to form a stronger complex with the  $\text{Cr}_2\text{O}_7^{=}$ .

In the discussion so far, the concentration in moles per 1000 grams of solvent has been used in place of the activity of the components. However in most cases the solutions are relatively dilute except for the experiments involving the higher lead concentrations. As mentioned earlier, there is little available information concerning the variation of activity with concentration and one is forced to speak only in the usual concentration units. As an alternative to the lead dichromate association explanation for the change in order of  $\text{Pb}^{++}$  ion, one might attribute the change to the variation of the activity coefficient of this ion as its concentration is increased. One can calculate the molal activity coefficient of  $\text{Pb}^{++}$  at some concentration assuming that the activity coefficient at 0.012 m is one and that the second order dependence in lead holds over the entire concentration ranges involved. One calculates from kinetic data that the activity coefficient is 0.66 at 0.050 m and 0.29 at 0.20 m  $\text{Pb}^{++}$  concentration. This calculation indicates that a rather rapid, although not unreasonable, change in activity coefficient with concentration is occurring. To decide whether one of these or some other explanation applies here will require more information than is available at present.



### Comparison of barium and calcium rates with theory

According to the mechanism given above, one should be able to calculate the solubility product of barium chromate from kinetic data. If one assumes that very little association between barium and dichromate occurs one gets a value from the kinetic data of the barium-dichromate reaction which is in good agreement with the value determined by direct chemical analysis. The solubility product of calcium chromate calculated from kinetic data is considerably less than the value obtained by direct chemical analysis. However the decrease in rate with calcium is in the right direction and possibly other factors such as water catalysis<sup>1</sup> enter in when the rate is extremely slow as it is with calcium. (Table 7).

### The temperature coefficient of the reaction

The temperature coefficient of the rate of the dichromate reaction cannot be analyzed in detail. However on the basis of what is known, the small temperature effect is not surprising. The slope of  $\log K_s$  against reciprocal temperature plot ( $K_s$  = solubility product of lead chromate in fused sodium nitrate-potassium nitrate) gives a value of 27 kcal per mole

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<sup>1</sup>Water appears to be particularly difficult to remove from some fused calcium salts (44).

Table 7. Comparison of solubility products of chromates obtained from kinetic data and direct chemical measurement

Chromate salt	Solubility product ( $K_s$ )	
	Kinetic data <sup>a</sup>	Chemical measurement <sup>b</sup>
$\text{BaCrO}_4$ (two expts.)	$6.3 \times 10^{-6}$	$4.0 \times 10^{-6}$
	$4.7 \times 10^{-6}$	
$\text{CaCrO}_4$	$0.12 \times 10^{-4}$	$1.7 \times 10^{-4}$

<sup>a</sup>Solubility product calculated from the equation

$$K_{s(M)} = \left\{ \frac{k'_{\text{Pb}} K_s^2(\text{Pb}) (M^{++})^2 [1 + 47(\text{Pb}^{++})]}{k'_M (\text{Pb}^{++})^2} \right\}^{\frac{1}{2}}$$

where  $k'$  = pseudo first order rate constant for the metal indicated by subscript

$K_s$  = solubility product

and  $M$  = barium or calcium.

<sup>b</sup>This research (see next section).

for the heat of solution of lead chromate. This should cause a considerable increase in rate but other heat effects, mainly that due to Reaction 17, are likely large and in the opposite direction so that the net effect is a very small rate dependence upon temperature. The heat of association of lead dichromate is apparently quite small as indicated by the small difference in the pseudo first order rate constants at 250° and 300°C compared at two different lead concentrations.

### The chloride effect

The chloride effect shown in Figure 6 is what one might predict on the basis of the explanation given above for the dichromate reaction and the values of the stability constants for the lead chloride complex ions in this solvent. As shown in Table 6 the addition of chloride ion has a small accelerating effect on the rate of the barium-dichromate reaction whereas with lead there is a marked retarding of the rate due to the addition of chloride. The solubility results show that chloride has little effect on the barium chromate solubility in this fused nitrate solvent whereas the solubility of lead chromate increases markedly. This effect was attributed to the formation of stable lead chloride complex ions and values were calculated for the various stability constants as shown in Table 13 in the next section.

Using the values for the lead chloride complexes at 300°C as evaluated from solubility data, one can calculate the  $\text{Pb}^{++}$  concentration expected under the conditions used in the kinetic experiments. The  $\text{Pb}^{++}$  concentration in solutions containing from 0.25 m to 1.00 m chloride was calculated using the lead chloride constants<sup>1</sup>,  $\beta_n$ , and the equation

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$$\beta_n = \frac{\text{PbCl}_n^{2-n}}{(\text{Pb}^{++})(\text{Cl}^-)^n}$$

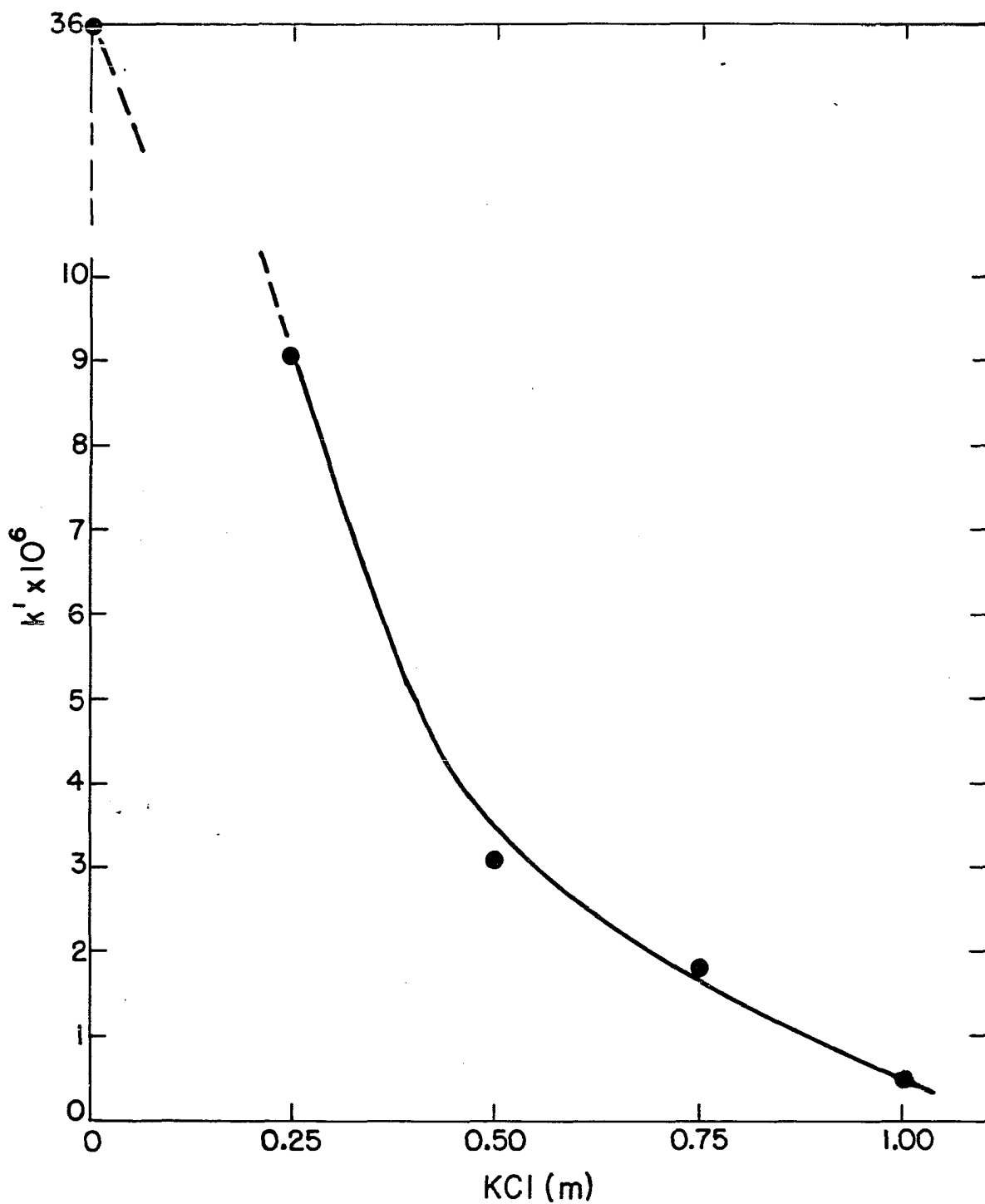


Figure 6. Dependence of pseudo first order rate constant on chloride concentration.  $\text{Pb}(\text{NO}_3)_2$   $t = 0.048$  m;  $\text{N}_2$  flow rate = 0.21 liters per min.; 95 grams solvent;  $300^\circ\text{C}$

$$(\text{Pb}^{++}) = (\text{Pb}^{++})_t / \left[ 1 + {}_1(\text{Cl}) + {}_2(\text{Cl})^2 + {}_3(\text{Cl})^3 \right] \quad (27)$$

These calculations take in account the appreciable amount of chloride tied up in lead chloride complexes. The values for the  $\text{Pb}^{++}$  concentration calculated in this manner are entered in column 4 of Table 8. The apparent lead concentrations, calculated from the kinetic data using the equation,

$$\frac{(\text{Pb}^{++})^2}{1.47(\text{Pb}^{++})} = \frac{k'}{0.051} \quad (28)$$

are given in column 5, Table 8.

Table 8. Comparison of lead ion concentration in solutions containing chloride calculated from solubility data and kinetic data

KCl m	$k' \times 10^5$ sec <sup>-1</sup>	$(\text{Pb}^{++})_t$ m	$(\text{Pb}^{++})_m$	
			Solubility data	Kinetic data
0.00	3.60	0.046	0.046	0.046
0.25	0.91	0.048	0.016	0.018
0.50	0.31	0.048	0.007	0.0094
0.75	0.18	0.048	0.003	0.0070
1.00	0.043	0.048	0.0013	0.0030

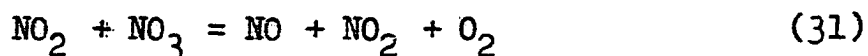
A comparison of these calculated values shows that the agreement is fairly good for the lower chloride concentrations and differs by a factor of about two at the higher concentrations. The agreement is still within experimental error however when one considers the large error involved in evaluat-

ing the stability constants for the complex species  $\text{PbCl}_2$  and  $\text{PbCl}_3^-$ . The cause of the slight acceleration in rate due to chloride in the case of the  $\text{Ba}^{++} + \text{Cr}_2\text{O}_7^{=}$  reaction is not known. If one assumes that the same catalytic effect is taking place in the case of lead, a correction for this effect would give better agreement between the values for the  $\text{Pb}^{++}$  concentration calculated from kinetic and solubility data.

### The bromide effect

The accelerating effect of bromide on the rate of this reaction has been mentioned. The fact that bromide ion was oxidized was also noted. In view of the explanation proposed for this reaction, a possible explanation for the bromide effect lies in the fast removal of one of the products of the equilibrium Reactions 17 or 18.

The mechanism for the decomposition of  $\text{N}_2\text{O}_5$  according to Ogg (45) is in accord with most of the available knowledge concerning this reaction. The mechanism involves the four reactions



The Reactions 29 and 30 represent a readily attained equilibrium between  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$  and  $\text{NO}_3$  and are followed by the bimolecular rate determining Reaction 31 which is in turn followed by the rapid Reaction 32 between  $\text{N}_2\text{O}_5$  and  $\text{NO}$ .

The accelerating effect of bromide ion could result from its oxidation by the powerful oxidizing  $\text{NO}_3$  group (46) or by the formation and rapid decomposition of nitryl bromide,  $\text{NO}_2\text{Br}$ . In either case, the much more rapid precipitation of chromate would result as observed.

The proposed mechanism of the reaction and the explanation for the large increase in rate when bromide is added suggests that an appreciable amount of bromide should be oxidized without any metal ion in solution to remove the chromate as it is produced. It was mentioned earlier that very little bromide was evolved without both  $\text{Pb}^{++}$  and  $\text{Cr}_2\text{O}_7^{=}$  ions present. These observations were made with fairly dilute bromide solutions (about 0.008 m). The following experiment was carried out to see if an appreciable amount of bromide is oxidized if it is added to a  $\text{K}_2\text{C}_2\text{O}_7$  solution in larger amounts. A 100 gram solution (300°C) containing 0.6 m  $\text{NaBr}$  and 0.012 m  $\text{K}_2\text{Cr}_2\text{O}_7$  was flushed with nitrogen for a period of 5 hours. A total of 0.20 milliequivalents of bromide was oxidized and at a rapidly decreasing rate. The rapidly decreasing rate suggests the build up of chromate ion in the

system. These facts support the existence of the equilibrium represented by Reaction 17.

### Acid-base interpretation of the dichromate reaction

Acid-base definitions are available which allow one to discuss almost all chemical reactions as acid-base reactions (47). The Lux (48) acid-base definition for oxide systems can be used profitably to discuss the dichromate reaction. The formulation



and the constant

$$K_{ab} = \frac{a_{\text{acid}} a_{\text{O}^{=2}}}{a_{\text{base}}} \quad (34)$$

are used to define and measure the strength of an acid-base pair. This treatment has been extended and developed by Flood and his coworkers (29, 30, 49, 50 and other papers) in studies of systems involving oxides and salts of oxy-acids.

In terms of the Lux concept, the equilibrium of the  $\text{Cr}_2\text{O}_7^{=2}$  and  $\text{NO}_3^-$  reaction would depend upon the relative values of the acid-base constant,  $K_{ab}$ , for the two equilibria:



and





The greater acidity of the  $\text{NO}_2^+$  ion relative to the  $\text{Cr}_2\text{O}_7^{=}$  would cause the equilibrium of Reaction 17 to lie to the left.

The pyrobridged salt,  $\text{Na}_4\text{P}_2\text{O}_7$ , when treated with fused alkali nitrates containing  $\text{Pb}^{++}$  ion produces a rapid evolution of nitrogen dioxide from the melt. It is possible that the same type of equilibrium proposed for the dichromate reaction might also be part of the mechanism of this reaction. In this case the relative rates would be a measure of the acidity of the different oxygen-bridged anions in a fused nitrate system. Although a more rapid reaction was obvious for the pyrophosphate salt, a knowledge of the concentrations and solubilities involved is necessary before one can compare the acid-base strength of the pairs. This kinetic method of comparing acid strength is analogous to one comparing the acidity of hydrogen acids in aqueous solution by observing the rate of hydrolysis of esters (36).

The studies of the equilibria resulting from the decomposition of pure fused pyrobridged anion salts have been mentioned in the Literature Review. Flood and Forland (29) suggest that the dependence of the equilibrium,



on the cation present results from the greater degree of coordination with oxy-anions with decrease in ionic size and increase in polarizing power of the cation. The importance of cation radius is shown by the fact that the stability of

the pyrosulfate increases with increase in radius in the cations  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ . The polarizing effect is shown by the fact that  $\text{Ag}_2\text{S}_2\text{O}_7$  is less stable than  $\text{Na}_2\text{S}_2\text{O}_7$  and  $\text{Tl}_2\text{S}_2\text{O}_7$  is less stable than  $\text{K}_2\text{S}_2\text{O}_7$ . It was mentioned that the same cation effect is indicated in studies of the dichromate equilibrium represented by Equation 9.

It is possible that the cations present might affect the equilibrium between  $\text{Cr}_2\text{O}_7^{=}$  and  $\text{CrO}_4^{=}$  in fused nitrates by analogy to the results above. In fact, the purpose of studying the rate of the  $\text{Cr}_2\text{O}_7^{=}$  and  $\text{Pb}^{++}$  reaction with either  $\text{Ba}(\text{NO}_3)_2$  or  $\text{Cd}(\text{NO}_3)_2$  added was to see if an effect on the equilibrium could be detected by comparing the rate data. A reduced rate with these added cations indicates a reduction in the  $\text{Cr}_2\text{O}_7^{=}$  activity whereas an enhanced rate indicates a reduction in the  $\text{CrO}_4^{=}$  activity, other things being equal. The reduced rate was observed with both cadmium and barium which means that the equilibrium is affected in the opposite sense than one might predict from the results of the work of Flood and his co-workers.

Greater changes in the composition of the nitrate melt with respect to the cations present might reveal interesting trends regarding the effect of cations on the equilibrium of Reaction 17. These possibilities suggest extensions of the type of kinetic studies discussed in this investigation. One big difficulty to overcome would be to affix the cause of the

added cation effect to either the equilibrium processes or to the rate-controlling step, the loss of gaseous equilibrium products. Some indications as to the nature of this cation effect might result from bromide oxidation studies since in this case the loss of gaseous equilibrium products by mass transfer appears to be small.

The preliminary bromide oxidation experiments were discussed earlier and a cation effect was mentioned (see Figure 1). From the discussion above, it is apparent that an appreciable cation effect on the  $\text{Cr}_2\text{O}_7^{=}$  and  $\text{CrO}_4^{=}$  equilibrium might reduce the concentration of the oxidizing species and thus reduce the rate of bromide oxidation as observed. On the other hand, if the added cation affects the rate-controlling mass transfer process in the absence of bromide, then its rate effect with bromide present might be attributed to the formation of less reactive bromide complexes. Information which would be helpful in interpreting these effects is the affect of barium and other cations on the rate of the bromide oxidation reaction.

## SOLUBILITY STUDIES

## Experimental

Materials and procedure

The solubility investigations involved measuring the increase in solubility of slightly soluble metal chromates in fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic solvent as halide ion was added.

A.C.S. reagent grade chemicals were used except where otherwise noted. The chromate salts of barium, calcium, lead, and magnesium were precipitated from aqueous nitrate solutions with a potassium chromate solution. Cadmium chromate was prepared by mixing solutions of stoichiometric amounts of cadmium nitrate and potassium chromate dissolved in the eutectic solvent. The solvent was then drawn off and the precipitate equilibrated with a second portion of the fused solvent. After the second portion of solvent had been drawn off, the cadmium chromate-solvent residue was used for the cadmium chromate solubility studies. A portion of the powdered residue was treated with water to dissolve off the nitrates and then the lemon-yellow precipitate was collected on a filter and washed with a small amount of water. After drying at  $110^\circ\text{C}$ , three samples were weighed out and analyzed for chromate content. The equivalent weight corresponded to  $78.2 \pm 1.7$  ( $\text{CdCrO}_4 = 76.1$ ). This, along with the fact that the chromate concentration of the solvent from which the pre-

precipitate was formed corresponded to the chromate solubility of the  $\text{CdCrO}_4$ -solvent residue in the eutectic, was considered evidence that the precipitate in the fused solvent was  $\text{CdCrO}_4$ .

The solubilities of the chromate salts in the fused  $\text{KNO}_3$ - $\text{NaNO}_3$  were determined in the following manner. An amount of the chromate salt in excess of its solubility was added to 50 grams of the fused solvent in a test tube. The test tube was immersed in a fused salt bath maintained at the desired temperature  $\pm 1^\circ\text{C}$  using a Merc-to-Merc Thermoregulator, Precision Scientific Company, Chicago, Illinois. The solutions were stirred from 15 to 30 minutes and then the excess chromate salt was allowed to settle. Usually one hour was allowed and was sufficient settling. A medicine dropper was used to withdraw samples which were then analyzed for their chromate and halide content. The absence of undissolved particles of the chromate salts in excessive amounts was reasonably assured by visual observation of the molten sample. The solutions were then stirred again for one-hour periods by a motion of a stirring rod operated mechanically and samples again withdrawn. The constancy of the chromate concentration within the experimental error of the measurement indicated that the desired equilibrium was attained<sup>1</sup>. The lower limit of chro-

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<sup>1</sup> $\text{CdCrO}_4$  attained equilibrium slowly on lowering temperature.

mate concentration to which this method could be used without the suspended precipitate amounting to more than one per cent of the measured chromate concentration is about  $10^{-4}$  m. This is indicated by the data in Table 9 in which the solubility of lead chromate in a fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic is depressed by the addition of  $\text{Pb}(\text{NO}_3)_2$ . There is little decrease in the

Table 9. Depression of  $\text{PbCrO}_4$  solubility with  $\text{Pb}(\text{NO}_3)_2$  in fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic at  $250^\circ\text{C}$

$\text{Pb}(\text{NO}_3)_2$ m	Chromate concentration m $\times 10^4$
0.00	$2.2 \pm 0.10$
0.025	$0.06 \pm 0.03$
0.100	$0.05 \pm 0.03$

measured chromate concentration in going from 0.025 m to 0.10 m  $\text{Pb}(\text{NO}_3)_2$ . This is probably because the amount of  $\text{PbCrO}_4$  suspended in the solution is of the same order of magnitude as the true solubility.

The chromate content of the samples at low concentrations was determined using the diphenylcarbazide colorimetric method (51). The one to two gram samples were weighed and then dissolved in 0.3N HCl in volumetric flasks. A one per cent by volume quantity of color reagent was added and the solution filled to the mark with more 0.3N acid. The color reagent

was prepared by dissolving four grams of phthalic anhydride and 0.25 grams of s-diphenylcarbazine (The Matheson Co., Inc., East Rutherford, N. J.) in 100 ml of 95 per cent alcohol. The colorimetric determination was made at a wave length of  $540\text{ m}\mu$  using a Coleman Junior Spectrophotometer. The concentration of chromate in a solution could be determined to within 2 per cent by the colorimetric method over the part of the calibration curve used in these experiments. The chromate concentration in the more soluble cases was determined by the iodine-thiosulfate method (33).

All of the chloride determinations were made using the Mohr method. Usually, unless the solutions were prepared by weight, only two determinations were made of the chloride concentration since this was found to remain constant for any particular solution. In most of the results with  $\text{PbCrO}_4$  and bromide and with  $\text{CdCrO}_4$  the solutions of known halide concentration were prepared by weight.

#### $\text{PbCrO}_4$ and $\text{CdCrO}_4$ solubilities

The effect of chloride on the solubility of  $\text{PbCrO}_4$  was determined at  $250^\circ\text{C}$ ,  $275^\circ\text{C}$  and  $300^\circ\text{C}$  and up to the limiting solubility of chloride in the eutectic melt at those temperatures. The solubility of lead chromate at the corresponding temperatures and chloride concentrations are shown in Table 10. For each entry, the mean deviation of the determinations

Table 10.  $\text{PbCrO}_4$  solubility dependence on temperature and chloride concentration in  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic solvent

250°C			275°C			300°C		
NaCl	$\text{PbCrO}_4$	No. <sup>a</sup>	NaCl	$\text{PbCrO}_4$	No.	NaCl	$\text{PbCrO}_4$	No.
(m)	$\text{m} \times 10^4$		(m)	$\text{m} \times 10^4$		(m)	$\text{m} \times 10^4$	
0.00	$2.2 \pm 0.1$	10	0.00	$4.1 \pm 0.3$	8	0.00	$6.6 \pm 0.2$	6
0.100	4.6	1	0.20	$4.6 \pm 0.5$	2	0.054	$8.5 \pm 0.9$	3
0.103	$3.7 \pm 0.3$	4	0.100	6.2	1	0.071	$7.7 \pm 0.6$	2
0.113	$4.9 \pm 0.2$	4	0.113	$6.2 \pm 0.1$	3	0.075	$7.6 \pm 0.3$	2
0.258	$7.5 \pm 0.5$	3	0.202	$8.0 \pm 0.6$	2	0.094	$7.6 \pm 0.3$	2
0.300	8.6	1	0.258	$10.2 \pm 0.3$	4	0.115	$11.2 \pm 0.9$	5
0.400	$10.0 \pm 1.0$	6	0.305	10.6	1	0.258	$14.3 \pm 0.7$	5
0.600	14.8	1	0.396	$13.3 \pm 0.9$	4	0.396	$18.6 \pm 2.3$	4
0.645	$14.9 \pm 0.1$	2	0.410	$12.6 \pm 0.1$	2	0.466	$24.4 \pm 0.9$	3
0.710	$17.6 \pm 1.2$	4	0.600	17.3	1	0.615	$24.2 \pm 4.9$	4
			0.654	$20.2 \pm 0.9$	6	0.705	$27.0 \pm 2.0$	4
			0.875	$24.6 \pm 2.9$	5	0.924	$44.5 \pm 4.0$	4
			0.904	$28.0 \pm 1.5$	7	1.00	$42.4 \pm 11.0$	2
						1.10	$55.0 \pm 0.9$	2

<sup>a</sup>No. indicates the number of determinations.



at each concentration is given (number of determinations given in next column). The corresponding data for the solubility of  $\text{PbCrO}_4$  in solutions containing bromide are shown in Table 11. At least three and up to six different solutions were used for the solubility determinations in the pure solvent. The equilibrium concentration was attained rapidly whether the temperature was approached from above or below.

Table 11.  $\text{PbCrO}_4$  solubility dependence on temperature and bromide concentration in  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic solvent

NaBr (m)	$\text{PbCrO}_4$ solubility ( $\text{m} \times 10^4$ )					
	250°C		275°C		300°C	
	m	No. <sup>a</sup>	m	No.	m	No.
0.00	$2.2 \pm 0.1$	10	$4.1 \pm 0.3$	8	$6.6 \pm 0.2$	6
0.005	$4.0 \pm 0.3$	2	$6.0 \pm 0.6$	2	$7.8 \pm 1.3$	2
0.10	$5.6 \pm 0.6$	2	$8.3 \pm 1.9$	4	$10.4 \pm 0.7$	5
0.20	$8.0 \pm 0.9$	2	$10.3 \pm 0.7$	4	$13.0 \pm 1.9$	5
0.30	$9.1 \pm 0.6$	2	$11.1 \pm 0.7$	3	$16.0 \pm 1.4$	2
0.40	$12.1 \pm 0.9$	2	$14.0 \pm 1.0$	3	$21.2 \pm 3.7$	2
0.60	$19.3 \pm 0.6$	2	21.2	1	$35.6 \pm 4.6$	2

<sup>a</sup>No. indicates the number of determinations.

In addition to the values reported in the tables, the  $\text{PbCrO}_4$  solubility in the pure solvent at 320°C was found to be  $9.9 \pm 0.3 \times 10^{-4}$  molal.

The effect of chloride and bromide on the solubility of  $\text{CdCrO}_4$  is shown in Table 12. The  $\text{CdCrO}_4$  solubility in the

Table 12.  $\text{CdCrO}_4$  solubility dependence on temperature and chloride and bromide concentration in  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic solvent

NaCl	$\text{CdCrO}_4$	NaBr	$\text{CdCrO}_4$
m	$\text{m} \times 10^2$	m	$\text{m} \times 10^2$
0.00	$0.80 = 0.07^a$	0.00	$0.80 = 0.07$
0.05	$1.4^b$	0.05	0.94
0.10	1.7	0.10	1.6
0.15	2.6	0.15	2.1
0.20	3.2	0.20	2.6
0.38	3.9	0.30	3.3
0.50	6.2	0.39	4.1
		0.44	5.3
250°C			
0.00	$0.59 = 0.07^a$	0.00	0.59
0.40	2.9	0.40	3.4
0.60	4.0	0.60	4.2

<sup>a</sup>Results from six different solutions averaged.

<sup>b</sup>Results for each halide concentration represent the average of three determinations for one solution.

pure solvent represents data obtained by approaching the temperature from above and below. The remaining data were obtained by approaching the equilibrium temperature from below.

Solubility of alkaline earth chromates

Fewer solubility determinations were made with the alkaline earth chromates since little variation in solubility was observed with the addition of halide ion. The solubility data for the alkaline earth chromates are shown in Table 13.

Table 13. Solubility of alkaline earth chromates in fused  $\text{KNO}_3\text{-NaNO}_3$  eutectic containing halide ions

Chromate salt	Solubility $\text{m} \times 10^2$	Solvent
300°C		
$\text{BaCrO}_4$	$0.20 \pm 0.02$	pure eutectic
	0.25	0.41 m NaCl
	0.27	1.00 m NaCl
$\text{CaCrO}_4$	$1.3 \pm 0.1$	pure eutectic
	1.4	0.64 m NaBr
250°C		
$\text{MgCrO}_4$	$0.55 \pm 0.09$	pure eutectic
	0.44	0.36 m KCl
	0.67	0.71 m KCl
	0.47	0.23 m NaBr
	0.55	saturated NaBr solution

### Attempts to extend the solubility studies

In order to obtain a more complete picture of the solubility effects, attempts were made to extend the solubility studies to other anions. However, the instability of solutions of  $\text{PbCrO}_4$  with iodide and cyanide and the low solubility of fluoride in this solvent ( $0.08 \text{ m}$  at  $300^\circ\text{C}$ )<sup>1</sup> were limiting factors in the study of these possible complexing anions.

Attempts were made to include more cations in this study but these were unsuccessful. The main difficulty was the lack of stability of chromate solutions with ions such as  $\text{Zn}^{++}$  and  $\text{Co}^{++}$  present under the conditions used in these experiments.

### Discussion

#### Calculation of stability constants of complex ions

It is apparent from the data presented that the halide ions increase the solubility of  $\text{PbCrO}_4$  and  $\text{CdCrO}_4$  but do not affect the solubility of the alkaline earth chromates appreciably. The increase in solubility of a salt such as lead chromate in fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic can be interpreted on the basis of complex ion formation. If, using  $\text{PbCl}_2$  as an

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<sup>1</sup>This research, fluoride precipitated from aqueous solution as  $\text{PbClF}$  and weighed.

example, one assumes that stable complex ions of the type  $\text{PbCl}_n^{2-n}$  are formed, then the total lead ion concentration,  $(\text{Pb}^{++})_t$ , can be expressed as the sum,

$$(\text{Pb}^{++})_t = (\text{Pb}^{++}) + (\text{PbCl}^-) + (\text{PbCl}_2) + (\text{PbCl}_3^-) + \dots \quad (38)$$

or in terms of the free lead and chloride concentrations

$$(\text{Pb}^{++})_t = (\text{Pb}^{++}) + K_1(\text{Pb}^{++})(\text{Cl}^-) + K_1K_2(\text{Pb}^{++})(\text{Cl}^-)^2 + \dots \quad (39)$$

where  $K_n$  is the stability constant

$$K_n = \frac{(\text{PbCl}_n^{2-n})}{(\text{PbCl}_{n-1}^{3-n})(\text{Cl}^-)} \quad .$$

The solubility of lead chromate should vary with the halide concentration according to the equation

$$K'_s = K_s \left[ 1 + \beta_1(\text{Cl}^-) + \beta_2(\text{Cl}^-)^2 + \beta_3(\text{Cl}^-)^3 - \dots \right] \quad (40)$$

where  $K'_s$  is the apparent solubility product of lead chromate,  $K_s$  is the solubility product of lead chromate in the pure solvent, and  $\beta_n$  is defined as

$$\beta_n = \frac{(\text{PbCl}_n^{2-n})}{(\text{Pb}^{++})(\text{Cl}^-)^n} \quad . \quad (41)$$

The stability constants for the complex ions of lead were determined by the graphical method of obtaining successive intercepts (52). First, a plot of the quantity A or  $(K'_s/K_s - 1)/(\text{Cl}^-)$  against  $(\text{Cl}^-)$  was made and the value of the

first stability constant,  $K_1$ , was obtained from the intercept of this plot. Next, a plot of the quantity  $\frac{A-1}{K_1} / (Cl^-)$  against  $(Cl^-)$  was made and the intercept of this plot and its slope gave the second stability constant,  $K_2$ , and the product,  $K_2K_3$ , respectively. Thus to explain the lead chromate solubility data, the formation of complex ions up to  $PbCl_3^-$  was assumed. The stability constants for the cadmium complexes were obtained from the equation of the straight line drawn through the points of a plot of solubility versus halide concentration. The stability constants for the complex ions are shown in Table 14. The estimated probable errors for the constants  $K_1$ ,  $K_2$  and  $K_3$  are 20, 50, and 100 per cent respectively. These uncertainties were estimated by plotting the data several times and averaging the values obtained (53).

#### Discussion of solubility results

The results of the solubility studies and the interpretation of these results show that both  $Pb^{++}$  and  $Cd^{++}$  are complexed by the halide ions,  $Br^-$  and  $Cl^-$ , in fused  $KNO_3$ - $NaNO_3$  eutectic solvent. No appreciable amount of complexing of the alkaline earth cations,  $Mg^{++}$ ,  $Ca^{++}$  and  $Ba^{++}$ , by these same halide ions is indicated. The  $Cd^{++}$  complexes with  $Br^-$  and  $Cl^-$  are of equal stability and more stable than the corresponding  $Pb^{++}$  complexes. The lead ion,  $Pb^{++}$ , forms slightly more stable complexes with  $Br^-$  than with  $Cl^-$ .

Table 14. Stability constants<sup>a</sup> for metal-halide complex ions in fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic solvent

Complex species	Stability constant		
	250°C	275°C	300°C
$\text{PbCl}^+$	18	8	6
$\text{PbCl}_2$	2	3	2.8
$\text{PbCl}_3^-$	2	1	1
$\text{PbBr}^+$	18	13	11
$\text{PbBr}_2$	5	2	2
$\text{PbBr}_3^-$	1	1	2
$\text{CdX}^+$	20	-	24
$\text{CdX}_2$	5	-	5
$\text{CdX}_3^-$	-	-	-

$$^a \text{Stability constant} = K_n = \frac{(\text{MX}_n^{2-n})}{(\text{MX}_{n-1}^{3-n})(\text{X}^-)}$$

where  $\text{X}^-$  is either  $\text{Cl}^-$  or  $\text{Br}^-$ .

The stability of the monohalide complexes of  $\text{Pb}^{++}$  decreases with an increase in temperature. The heats of association for the  $\text{PbCl}^+$  and the  $\text{PbBr}^+$  complexes are  $8 \pm 3$  and  $5 \pm$  kcal. per mole respectively. The temperature effect on the other complexes cannot be evaluated from solubility data.

Qualitatively, the important conclusions from the solubility data are in good agreement with the results of Van Artsdalen (15) (see Table 1, p. 13) in regard to the cations which are complexed and the stability of the complex ions in a

fused salt. The solvent used in this investigation is essentially the same except for the substitution of half of the  $\text{Na}^+$  with  $\text{K}^+$  cations. The effect due to this change in cations is presumably small although there is evidence for an increase in stability of possibly similar complex ions in fused salts with increase in size of the alkali metal ion present (3).

One difference in the conclusions is the claim regarding the complex species which are important, i.e., those which are present in appreciable concentrations in the fused salt solvent. Van Artsdalen states that only the complexes containing an even number of ligands are important whereas the results of this investigation are interpreted in a manner such that all of the complex ions formed in a stepwise process are important. The basis for Van Artsdalen's claim has been mentioned. The justification for using the stepwise process should be mentioned.

If one attempts to explain the solubility behavior on the assumption that only complex ions containing an even number of halide ions are important, then the second constant,  $\beta_4$  turns out negative. A negative value is of course meaningless according to the definition of the constant.

The stepwise process is essentially the simplest type of complex ion formation which one might assume and it is analogous to the complexing behavior of the same ions in aqueous solutions.  $\text{Pb}^{++}$  forms the positively charged mono-



halide complex with bromide and chloride in aqueous solutions as shown by conductometric studies (54) and more convincingly by spectrophotometric studies (55). The complexing of  $\text{Cd}^{++}$  with chloride ion in aqueous solutions is interpreted in terms of the stepwise formation of complex ions and in this case the stability constant,  $K_n$ , decreases with increase in the number of halide ions in the complex.

The large difference in the stability of the complexes of  $\text{CdBr}_2$  and  $\text{CdCl}_2$  observed by Van Artsdalen in the freezing point studies was not observed in the solubility study. The freezing point studies indicated a much greater degree of complexing with  $\text{CdBr}_2$  than with  $\text{CdCl}_2$ . Possibly aggregation of the complex ions in the case of  $\text{CdBr}_2$  is occurring which would have the effect of reducing the number of particles observed by a freezing point depression measurement but would not affect the solubility relationship. The freezing point data would then indicate a greater degree of association.

A similarity in the two solvents, fused alkali nitrates and water, is noted on comparing the stabilities of the metal halide complex ions in the two solvents. Values for the stability constants of metal halide complexes in the two solvents are listed in Table 15 for comparison. This similarity is a reflection of the solvating characteristics of two solvents. Irving and Williams (56) state that the ligands,  $\text{I}^-$ ,  $\text{Br}^-$  and  $\text{Cl}^-$  among others show weak interactions with metals

Table 15. Stability constants of complex ions in water and fused  $\text{KNO}_3$ - $\text{NaNO}_3$  eutectic

Complex ion	Stability constant ( $K_n$ )	
	In water (25°C)	In fused nitrates <sup>a</sup>
$\text{PbCl}^+$	27 <sup>b</sup>	6
$\text{PbBr}^+$	17	11
$\text{CdCl}^+$	23 <sup>c</sup>	24
$\text{CdCl}_2$	2.5	5

<sup>a</sup>At 300°C.

<sup>b</sup>Values for lead from ref. 55.

<sup>c</sup>Ionic strength = one. Values for cadmium from ref. 53.

because the heat of formation of the metal-ligand bond is comparable with, or less than, the heat of formation of a metal-water bond. The fact that there is a neutralization of positive charge and a resultant entropy gain offsets the loss of interaction energy which occurs when water is replaced by a ligand. In the fused nitrate solvent, the replacing of a solvating nitrate ion with one of the ions above does not involve a neutralization of charge and thus one reasons that the formation of a stable complex ion is a result of a favorable heat of formation. The weaker interaction of the nitrate ion with metal ions is indicated by the small value ( $K=0.67$ ) (55) for the stability constant of  $\text{PbNO}_3^+$  in aqueous solution.

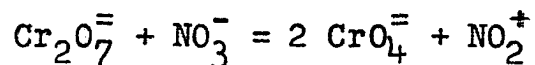
## SUMMARY

The results of this investigation have provided additional information by chemical methods of the extent of association in fused salts. Association effects observed in solubility and rate studies in fused alkali nitrate are shown to be consistent with the assumption that complex ions such as those existing in aqueous solutions are formed between metal ions and halide ions. In addition, the rate studies suggest a mechanism for a reaction involving dichromate and nitrate ions in a fused alkali nitrate solvent.

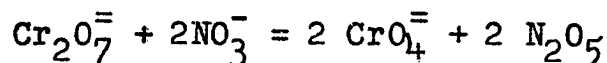
The interpretation of solubility dependence on halide concentration of metal chromate in a fused eutectic mixture of  $\text{KNO}_3$  and  $\text{NaNO}_3$  in terms of complex ion formation shows that:

- 1) The metal ions,  $\text{Pb}^{++}$  and  $\text{Cd}^{++}$ , are complexed by both chloride and bromide ions in the fused nitrate solvent and the alkaline earth ions,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$  and  $\text{Ba}^{++}$ , are not complexed to an appreciable extent.
- 2) The stability constants for the complex ions,  $\text{MX}^+$ ,  $\text{MX}_2$  and  $\text{MX}_3^-$ , are evaluated from the solubility data. The stabilities of the complex ions in the fused salt solvent are not greatly different from their stabilities in aqueous solutions. The complex ions,  $\text{PbCl}^+$  and  $\text{PbBr}^+$ , decrease in stability with increase in temperature.

The kinetic studies on the rate of precipitation of a chromate salt from a dichromate solution in fused alkali nitrates resulted in the following proposed mechanism for the reaction. The equilibrium



or alternately



is postulated to exist in the fused salt. The equilibrium lies far to the left but on the addition of a metal cation, notably  $\text{Pb}^{++}$ , which removes the chromate ion as it is formed, the reaction goes to completion at a measurable rate. The rate at which this reaction goes to completion is controlled by the rate at which the other equilibrium product, nitrogen pentoxide or its dissociation product, the nitronium ion, is removed from the solution either by evaporation or decomposition.

The rate dependence on chloride ion concentration is consistent with the mechanism proposed and the extent of complexing of  $\text{Pb}^{++}$  by  $\text{Cl}^-$  shown by the solubility data.

The discussion of the equilibrium reaction between the dichromate ion and nitrate ion in terms of an acid-base definition for oxide systems points out relationships between these kinetic studies and other equilibrium studies in fused salts.

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